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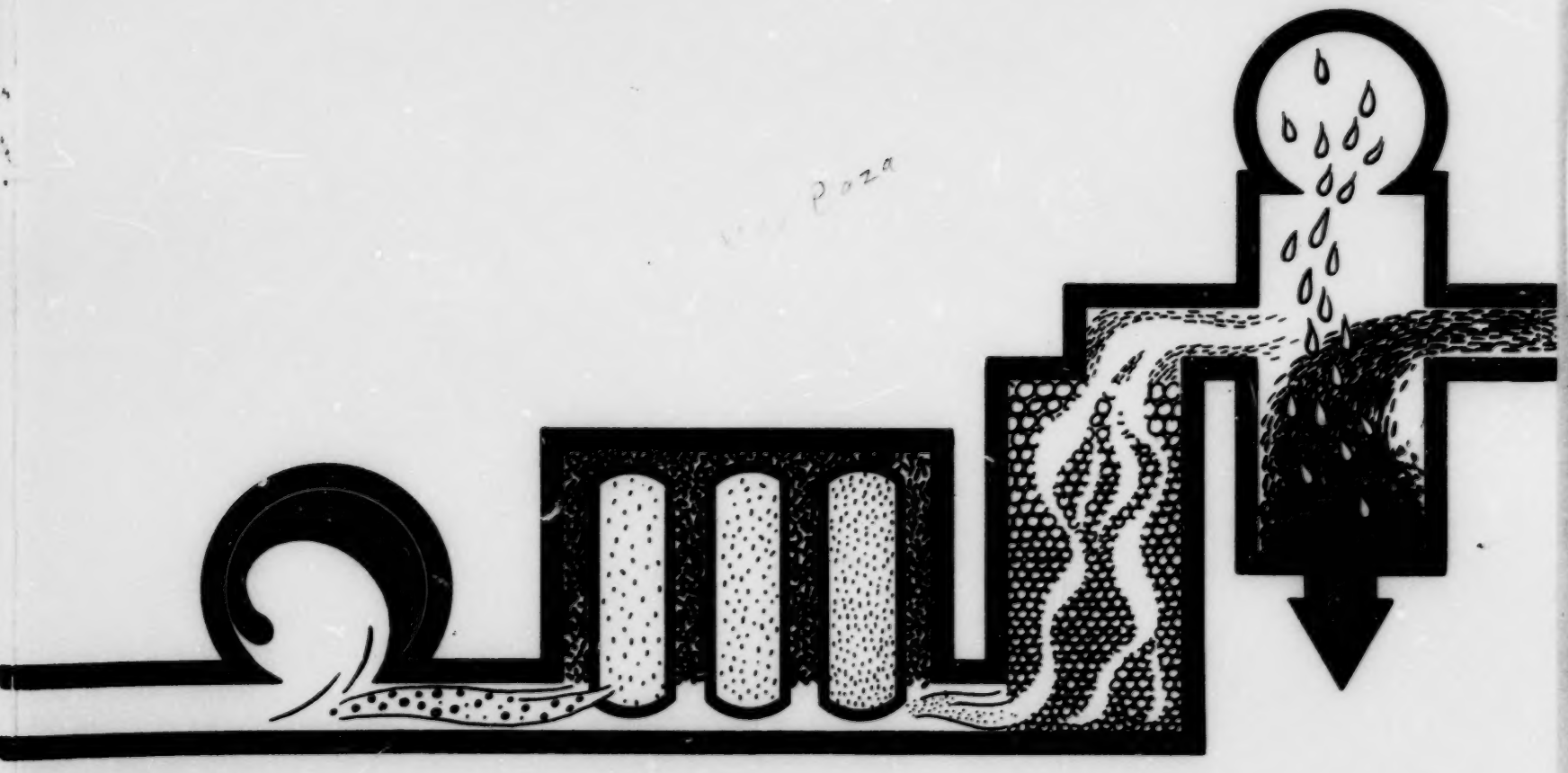
# ULTIMATE DISPOSAL OF PHOSPHATE FROM WASTE WATER BY RECOVERY AS FERTILIZER



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81

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27 Abstract

Many of the proposed processes that reduce orthophosphate in the effluents from sewage treatment plants result in the extracted phosphate being concentrated in the digester supernatant. This phosphate must be removed prior to disposal of the supernatant or its recycle back to the head of the treatment plant. Digester supernatant was treated in two ways. The first was to add magnesia and elevate the pH to 9 to cause precipitation of the phosphorus. The other technique was to apply heat and/or vacuum to the digester supernatant which caused precipitation of the soluble orthophosphate. A 90% removal of orthophosphate can be achieved by either approach. The heat and/or vacuum process also yields a supernatant substantially lower in BOD, COD, and nitrogen concentration. The precipitated phosphorous (primarily a mixture of calcium phosphate and magnesium ammonium phosphate) was found available for plant food according to AOAC (i.e., Association of Official Agricultural Chemists) procedures. Work was conducted by bench and pilot plant studies on digester supernatant from the Lake Zurich, Illinois sewage treatment plant and from the Libertyville, Illinois sewage treatment plant. (Selby-Texas)

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# ULTIMATE DISPOSAL OF PHOSPHATE FROM WASTE WATER BY RECOVERY AS FERTILIZER

by

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DEPARTMENT OF THE INTERIOR

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TABLE OF CONTENTS


| | Page |
|---|---|
| INTRODUCTION | 1 |
| EXPERIMENTAL | 3 |
| BACKGROUND | 4 |
| DIGESTER SUPERNATANT STUDIES | 6 |
| PROCESS DESCRIPTION | 6 |
| WASTE CHARACTERIZATION AND PLANT SELECTION | 9 |
| PRELIMINARY PRECIPITATION STUDIES | 9 |
| PRECIPITATION BY CHEMICAL ADDITION | 15 |
| Bench Scale Experiments | 15 |
| Pilot Plant Studies | 19 |
| PRECIPITATION BY HEAT DECOMPOSITION | 24 |
| Bench Scale Studies | 27 |
| Pilot Plant Studies | 35 |
| Batch Experiments | 35 |
| Continuous Experiments | 41 |
| EFFLUENT QUALITY | 47 |
| PRODUCT CHARACTERIZATION | 56 |
| SUMMARY AND CONCLUSIONS | 64 |
| PATENT DISCLOSURES | 66 |
| REFERENCES | 68 |
| APPENDIX | 70 |
| ANALYTICAL METHODS | 71 |

## ABSTRACT

Many of the proposed processes that reduce orthophosphate in the effluents from sewage treatment plants result in the extracted phosphate being concentrated in the digester supernatant. This phosphate must be removed prior to disposal of the supernatant or its recycle back to the head of the treatment plant.

Digester supernatant was treated in two ways. The first was to add magnesia and elevate the pH to 9 to cause precipitation of the phosphorus. The other technique was to apply heat and/or vacuum to the digester supernatant which caused precipitation of the soluble orthophosphate. A 90% removal of orthophosphate can be achieved by either approach. The heat and/or vacuum process also yields a supernatant substantially lower in BOD, COD, and nitrogen concentration.

The precipitated phosphorous (primarily a mixture of calcium phosphate and magnesium ammonium phosphate) was found available for plant food according to AOAC (i.e., Association of Official Agricultural Chemists) procedures.

Work was conducted by bench and pilot plant studies on digester supernatant from the Lake Zurich, Illinois sewage treatment plant and from the Libertyville, Illinois sewage treatment plant.

This report was submitted in fulfillment of Program No. 17070 ESJ, Contract No. 14-12-171, between the Federal Water Quality Administration and the Dearborn Chemical Division of W. R. Grace and Company.

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# INTRODUCTION

A conventional activated sludge or trickling filter sewage treatment plant with an anaerobic digester, produces a stream of digester supernatant which contains a high concentration of COD, BOD, nitrogen and phosphorus.

Digester supernatant is a troublesome stream because it normally is returned to the head of the plant, usually intermittently, causing a severe overloading of the plant. A process for the removal of phosphate from digester supernatant in a form that could be sold as a fertilizer is appealing because of the promise of sufficient monetary return to pay for the treatment costs and because ultimate disposal of the phosphorus results when it is returned to the soil. One approach which seems plausible is to precipitate and recover the phosphate from the digester supernatant as magnesium ammonium phosphate. This compound has a low solubility in water, thus assuring high recovery of phosphorus present in the waste streams as orthophosphate. Because of its low solubility, magnesium ammonium phosphate has been used in analytical chemistry for many years for the quantitative precipitation of phosphate. Its precipitation is the basis for a process for descaling sea water (1,2), i.e., removing magnesium and calcium from sea water prior to desalination and the production of fresh water. Therefore, with proper condition of pH, phosphate concentrations, etc., the precipitation and recovery of magnesium ammonium phosphate from digester supernatant seems feasible.

The agronomic properties of magnesium ammonium phosphate are excellent (3,4). It has a high percentage of highly available plant nutrients. Because of its low water solubility and, hence, "non-burning" properties, magnesium ammonium phosphate can command a premium price in certain fertilizer applications. If magnesium ammonium phosphate could be produced from the phosphate and ammonia in the digester supernatant, not only would a pollution problem be solved but the economics should be favorable for production of the fertilizer due to savings in raw material costs. It is postulated that revenue from the sale of the fertilizer would pay for the waste treatment costs and perhaps even return a small profit.

The research summarized in this report is concerned with a bench and pilot plant study to determine the feasibility of recovering phosphorus from digester supernatant in a form suitable for sale as a fertilizer ingredient.

Phase I of this project concerned the leaching of orthophosphate from waste activated sludge and formation of magnesium ammonium phosphate from this leachate. Details of that study have been presented in a Phase I Final Report. Due to the more practical considerations of the Phase II study the report of this phase will serve as the final report of the contract.

# E X P E R I M E N T A L

## BACKGROUND

Digester supernatant is a natural by-product of the conventional sewage sludge digestion process. The recent interest in nutrient control has resulted in many studies on the levels of phosphorus in various digester supernatants. The amount of total phosphorus in digester supernatant is primarily a function of the suspended solids present; whereas the orthophosphate concentration is more closely related to the type of sludge digested and the nature of the digester operation. For example, Shea (5) reports a digester supernatant having 17,000 mg/l suspended solids, contained 282 mg/l total phosphorus as P, of which 208 mg/l was in the orthophosphate form. Fisher (6) in a study of several treatment plants found total phosphorus concentrations ranging from 45 to 123 mg/l and found 66 to 84 percent of the phosphorus was in the orthophosphate form.

As new or "raw" sludge is pumped into a digester and mixes with the older digesting sludge, an equivalent volume of the liquid in the digester that contains the least amount of suspended solids must be pumped out. Kappe (7) discusses the troublesome nature of this material and points out the disadvantage of returning supernatant to the head of the waste treatment plant (which is still widely practiced today).

Many of the proposed processes that reduce orthophosphate in sewage treatment plant effluents result in the extracted phosphorus being concentrated in the digester. (Anaerobic release occurs in the digester and converts much of the phosphorus to soluble orthophosphate.) Unless this increased orthophosphate can be removed prior to recycle of the supernatant back to the treatment plant, the phosphate removal schemes presently under study would not be continually effective. Therefore, precipitation of phosphorus from digester supernatant has become extremely important. Barth (8) describes various treatment schemes to minimize the problem.

Precipitation of phosphate from the digester supernatant of an efficient activated sludge sewage treatment plant, is particularly interesting because most of the phosphate is concentrated in a volume lower than 1% of the total stream of the plant.

Rawn (9) in studying digestion in 1939, found crystalline material in a supernatant line, which was identified as magnesium ammonium phosphate. He felt this compound was too soluble to normally form under conditions found in a digester, and its presence was left unexplained. However, it appears that Rawn was wrong with regard to this solubility limitation.

The literature values shown in the following table indicate that solubility of magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$) in water at 25°C averages about 0.016 g/100 ml (i.e., 160 mg/l).

| | g/100 ml |
|---|---|
| Bridger, et al. (3) | 0.018 |
| Bube (10) | 0.017 |
| Szekeres and Rady (11) | 0.016 |
| Uncles and Smith (12) | 0.014 |
| Average | 0.016 |

All solubility determinations in the table were based on phosphate analyses except that of Uncles and Smith which was based on magnesium analysis. Expressed as phosphorus (P) the solubility is about 20 mg/l.

Since the concentration of orthophosphate P in digester supernatant generally exceeds 20 mg/l, precipitation of magnesium ammonium phosphate can normally be expected. Other conditions usually associated with a well-operated digester (i.e., a buffered system containing a high concentration of ammonium bicarbonate and other ammonium salts) further decrease the solubility of the compound.

The solubility of magnesium ammonium phosphate is dependent on pH. It increases rapidly as the pH is lowered but decreases as the pH is raised above 7. Very high pH (i.e., greater than 10) should be avoided because the compound decomposes to form trimagnesium phosphate, $Mg_3(PO_4)_2 \cdot 4H_2O$. The solubility of magnesium ammonium phosphate is greatly reduced by precipitation in an ammoniacal solution containing an excess of soluble magnesium and ammonium salts. This is the basis of a well-established analytical procedure for phosphate determination in which the solubility losses of phosphorus are reduced to only a few milligrams per liter.

If calcium salts are present, calcium will coprecipitate with the magnesium ammonium phosphate in various forms of calcium phosphate. Although phosphate removal is achieved by precipitation with calcium, the fertilizer value of the calcium phosphates is less than that of magnesium ammonium phosphate. Thus, the calcium concentration during precipitation of the magnesium ammonium phosphate should be as low as possible to prevent dilution of the product with less desirable phosphates.

## DIGESTER SUPERNATANT STUDIES

### PROCESS DESCRIPTION

Two processes were studied for the removal of phosphate from digester supernatant (DS); (1) precipitation by addition of magnesia or magnesium carbonate and a soluble base for pH adjustment, and (2) precipitation by heat and/or vacuum decomposition of ammonium bicarbonate for pH adjustment. The flow sheets for the two processes are shown in Figures 1 and 2.

In the first process, a slurry containing 5% to 10% magnesium hydroxide solids or magnesium carbonate is continuously metered into a pipe premixer where it prereacts with the DS. This mixture is further neutralized with sodium hydroxide to reach a pH of 9.0, in a reactor fitted with a high speed agitator. Continuous monitoring of pH is used as a control for the process. The retention time in the reactor should be approximately 10 minutes. The treated DS is discharged by gravity, directly to a continuous centrifuge or a conventional settler. The underflow from the settler is centrifuged or filtered. The solids are dried in a conventional rotary dryer.

The second phosphate precipitation process is based on the use of heat and/or vacuum to destroy the bicarbonate which is present in the DS. Evolution of $CO_2$ raises the pH effecting the precipitation of magnesium and calcium phosphates without the addition of chemicals. This process does not require additional chemicals when the DS of an area contains a high concentration of magnesium and calcium ions. In areas where the water is soft, (i.e., where the hardness is below that stoichiometrically needed to precipitate phosphate), then supplemental magnesia will be required.

A continuous flow of DS is pumped into a reactor where the temperature is raised to 65°-75°C. The reactor may be operated under a slight vacuum to enhance the stripping of $CO_2$. The retention time necessary for complete precipitation of phosphate is determined by the initial concentration of ammonium bicarbonate. The pH is monitored continuously and it should raise to 8.5 to 8.9 for optimum phosphate removal. A high degree of agitation is desirable to expose a large surface area and enhance $CO_2$ evolution. The treated DS is pumped into a continuous centrifuge or a conventional settler. The solids are dried in a conventional rotary dryer. As an alternative, a fraction of the solids prior to drying may be recycled to the reactor to increase the percent solids in the DS and enhance crystal growth. These two processes may be operated on a batch or a continuous basis.

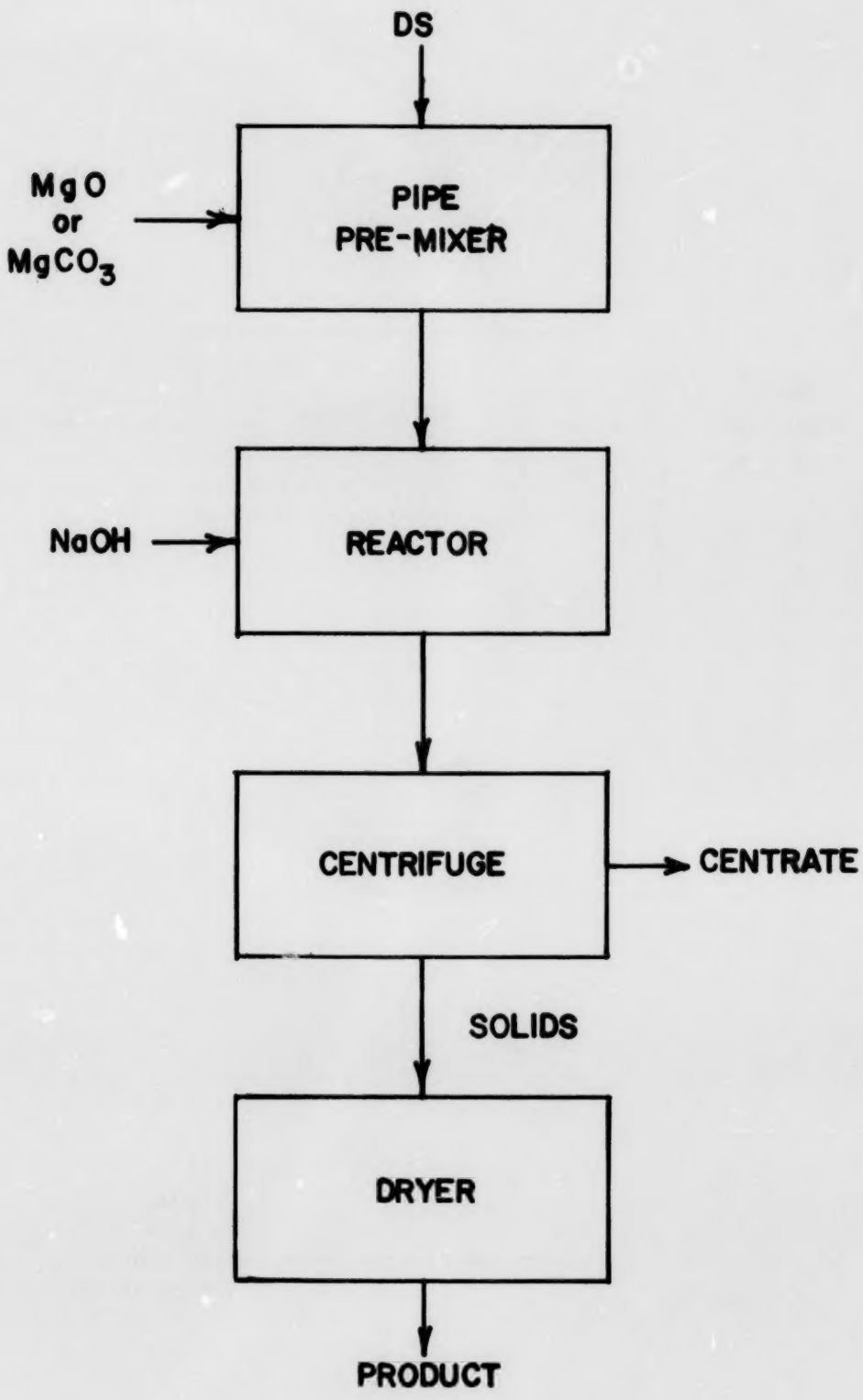



FIGURE 1. RECOVERY OF PHOSPHATE FROM DIGESTER SUPERNATANT BY ADDITION OF MAGNESIA OR MAGNESIUM CARBONATE AND SODIUM HYDROXIDE

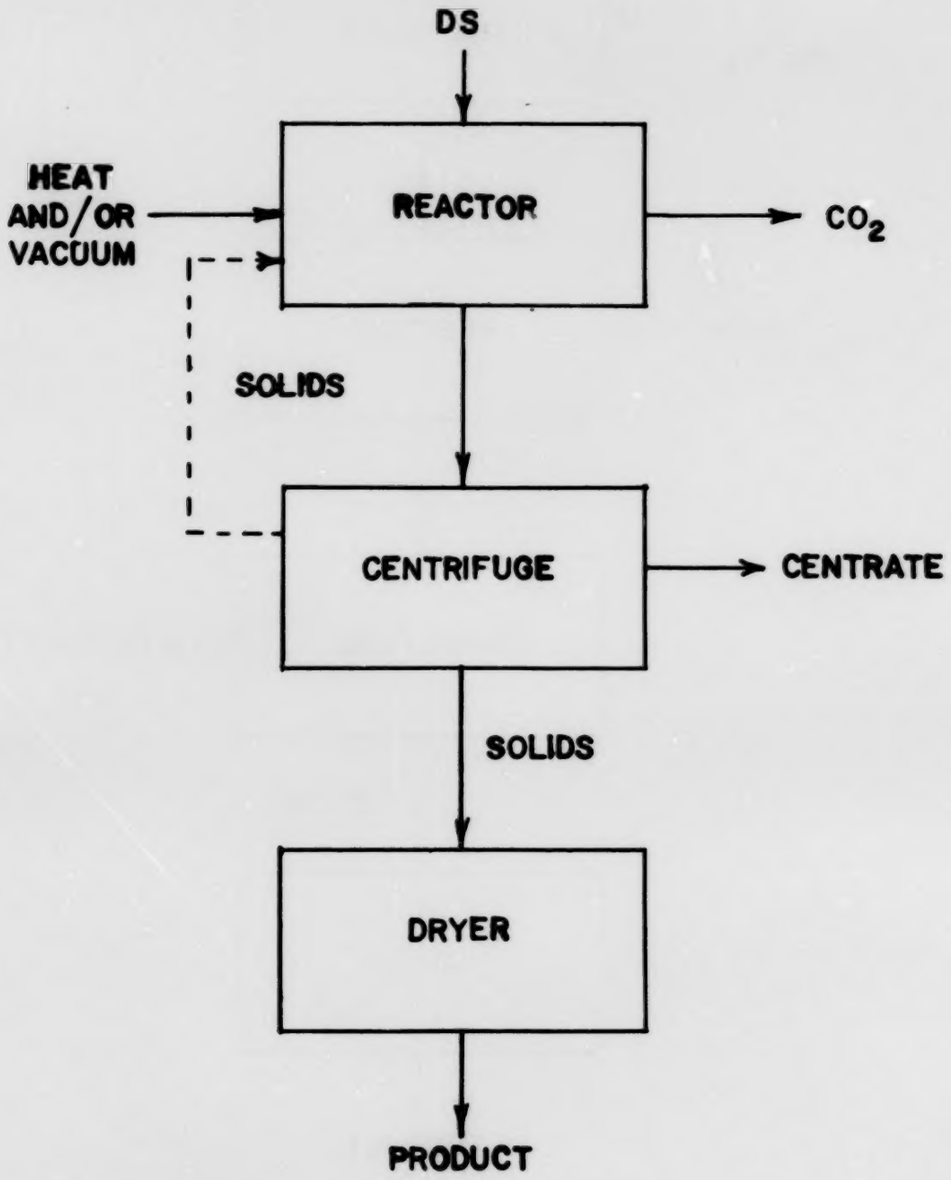



FIGURE 2 RECOVERY OF PHOSPHATE FROM DIGESTER SUPERNATANT BY DECOMPOSITION OF AMMONIUM BICARBONATE

## WASTE CHARACTERISTICS AND PLANT SELECTION

A study of local plants was made to obtain a suitable source of digester supernatant. A list of the plants surveyed follows:

| | |
|---|---|
| Barrington, Illinois | Lake Zurich, Illinois |
| Crystal Lake, Illinois | Libertyville, Illinois |
| Deerfield, Illinois | Mundelein, Illinois |
| East Dundee, Illinois | Wauconda, Illinois |
| Highland Park, Illinois | West Dundee, Illinois |

In Table I can be seen the analytical results for the DS samples obtained at the ten locations. All the research work was performed primarily with samples obtained from the Lake Zurich, Illinois and Libertyville, Illinois plants.

The Lake Zurich, Illinois plant is a trickling filter plant with a 500,000 gal/day capacity. The plant is operated at design load. The plant has a two-stage digestion system. The primary digester is circulated and heated; the secondary tank is under quiescent conditions to settle out the solids. The DS is returned from the secondary tank to the head of the plant. All the experiments were performed with samples from the secondary digester.

The Libertyville plant is a 1.5 mgd capacity conventional sludge plant which is operating at design capacity. Seventeen small manufacturing facilities contribute industrial waste to the sewage system. The plant has a two-stage digestion system, the primary digester which is heated, and a secondary tank for storage and further digestion under quiescent conditions. The DS is returned from the secondary tank to the head of the plant.

In Table II can be seen the average composition of the DS obtained from the secondary digester from the Lake Zurich and Libertyville sewage treatment plants. Samples were analyzed for a period of three months and one year respectively.

A schematic of the Lake Zurich and Libertyville sewage treatment plant can be seen in Figures 3 and 4.

## PRELIMINARY PRECIPITATION STUDIES

The main objective of this work was to develop optimum conditions for the precipitation of magnesium ammonium phosphate hexahydrate from a waste stream containing a phosphate concentration in the range of 50-100 mg/l P as orthophosphate. The precipitation was achieved by adding either a soluble salt of magnesium, solid magnesium oxide, a slurry of magnesium hydroxide or a solid magnesium carbonate. Final pH adjustment, when required, was achieved by adding a soluble base such as sodium hydroxide or ammonia.

TABLE I

DIGESTER SUPERNATANT CHARACTERIZATION
AT TEN LOCAL SEWAGE TREATMENT PLANTS

| Plant Location | Barrington | Crystal Lake | Deerfield | East Dundee | Highland Park | Lake Zurich | Libertyville | Mundelein | Wauconda | West Dundee |
|---|---|---|---|---|---|---|---|---|---|---|
| SS mg/l | 7,060 | - | 11,500 | 47,600 | 11,220 | 960 | 790 | 19,900 | 660 | - |
| COD mg/l | 7,720 | 4,550 | 13,386 | 45,590 | 2,907 | 2,632 | 1,900 | 17,860 | 6,203 | 35,200 |
| pH | 7.2 | 7.3 | 7.1 | 7.2 | 7.2 | 7.0 | 7.1 | 7.1 | 6.9 | 6.9 |
| $CO_2$ mg/l | - | - | 1,685 | 3,484 | 2,736 | 2,094 | 2,323 | 2,974 | 1,496 | - |
| TKN mg/l | 624 | 494 | 934 | 175 | 925 | 621 | 524 | 139 | 378 | 18 |
| Ammonia N mg/l | - | - | 404 | 65 | 768 | 509 | 445 | 64 | 332 | - |
| TP mg/l | 170 | 46 | 227 | 1,150 | 91 | 115 | 80 | 750 | 96 | 212 |
| OP mg/l | - | - | 62 | - | 73 | 51 | 61 | - | 57 | - |
| Ca mg/l | 136 | 150 | 496 | 2,077 | 163 | 190 | 142 | 1,112 | 203 | 115 |
| Mg mg/l | 78 | 7 | 128 | 398 | 58 | 73 | 79 | 262 | 100 | 30 |

SS - Suspended Solids
COD - Chemical Oxygen Demand
TKN - Total Kjeldahl Nitrogen
TP - Total Phosphorus
OP - Orthophosphate Phosphorus

TABLE II

AVERAGE COMPOSITION OF DIGESTER SUPERNATANT
FROM THE LAKE ZURICH AND LIBERTYVILLE
SEWAGE TREATMENT PLANTS

| | Lake Zurich | Libertyville |
|---|---|---|
| Suspended Solids (mg/l) | 1,518 | 740 |
| Total Phosphorus (mg/l as P) | 85 | 100 |
| Orthophosphate (mg/l as P) | 66 | 60 |
| Chemical Oxygen Demand (mg/l) | 2,230 | 1,230 |
| pH | 7.2 | 7.0 |
| $CO_2$ (mg/l) | 2,209 | - |
| TKN (mg/l as N) | 678 | 360 |

TKN - Total Kjeldahl Nitrogen

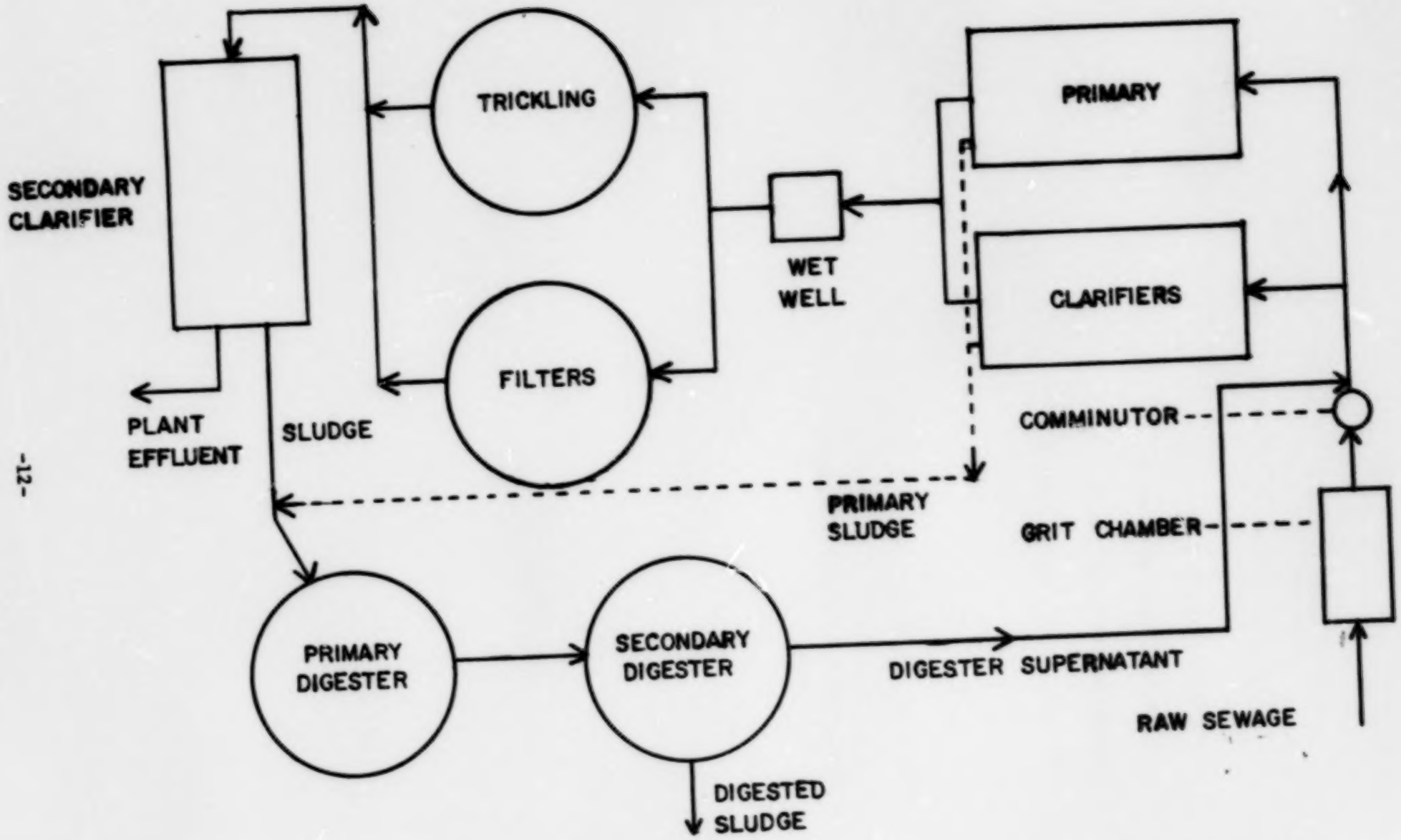



FIGURE 3. SCHEMATIC OF THE LAKE ZURICH, ILLINOIS SEWAGE TREATMENT PLANT

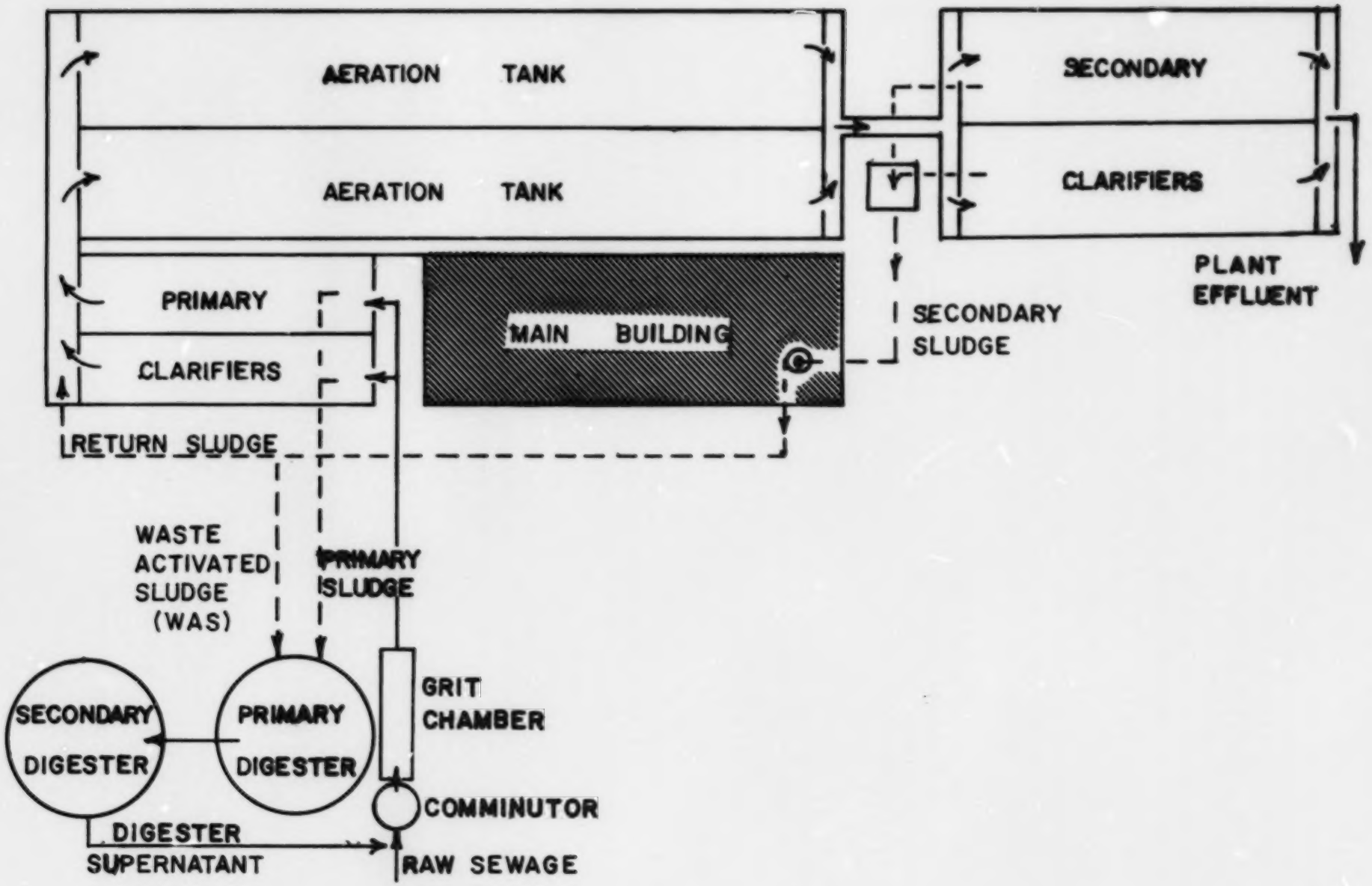



**FIGURE 4** SCHEMATIC OF THE LIBERTYVILLE, ILLINOIS, SEWAGE TREATMENT PLANT

An evaluation of the waste streams from the Lake Zurich and Libertyville sewage plants indicated that the water contained a large concentration of calcium, over 100 mg/l. Calcium reacts with orthophosphate to form either dicalcium phosphate, tricalcium phosphate or hydroxyapatite. In view of this condition, it became apparent that it was desirable to study the effect of calcium, at different concentrations, on the precipitation of magnesium ammonium phosphate. A synthetic mixture containing $Ca^{++}$, $Mg^{++}$ and $PO_4^{\equiv}$ ions in concentrations similar to those expected in a waste stream was used for the preliminary investigation.

The work on precipitation was not only concerned with the efficiency of phosphate removal from the stream but also with the type and quality of the precipitated solid because a process was visualized which would yield a solid by-product with economic value.

The general procedure used in these experiments is as follows: To 900 ml of deionized water was added a predetermined volume of stock solution containing (1) 10,000 mg/l of P prepared with phosphoric acid; (2) 10,000 mg/l of Mg prepared with magnesium sulfate and (3) 5,000 mg/l of Ca prepared with calcium chloride. Finally the volume of the sample was brought up to 1 liter. The sample was agitated at 400 rpm in a beaker fitted with pH electrodes. A soluble base, either a 10% solution of ammonium hydroxide or a 1N sodium hydroxide solution was used to bring the pH up to a predetermined level. Neutralization was performed in approximately 15 minutes. After reaching the desired pH level, the suspension was stirred for one hour to allow crystal growth and finally settled for a period of approximately one hour. The settled solids were filtered in a Buchner funnel using #5 Whatman paper. In some cases the solids recovered were difficult to filter, and then a fine fritted glass funnel or a centrifuge were used for the solid-liquid separation. The filtrates were analyzed for residual Ca, Mg, and P. The calcium and magnesium were determined by EDTA titration and the phosphate by the aminonaphtholsulfonic acid method. The solids were analyzed by X-ray and in some cases by standard AOAC (Association of Official Agricultural Chemists) procedures for total phosphate, available phosphate, nitrogen, calcium and magnesium.

Conclusions reached as a result of the preliminary precipitation studies (13) are as follows:

1. In a system free of calcium the recovery of phosphate depends on pH, increasing from 41% at pH 8.5 to 93% at 10.0. The precipitated solid is predominantly $MgNH_4PO_4 \cdot 6H_2O$.

2. In a system containing calcium, phosphate recovery is higher than that obtained at the same pH in its absence. The optimum pH is 9.5 yielding a phosphate recovery of about 98%, but the solid contains calcium phosphates in addition to the magnesium phosphates.

3. A high phosphate recovery (95%) is obtained at pH 9.0 when the

magnesium ion concentration is in excess, i.e., 25% or more above stoichiometry.

4. Calcium precipitates preferentially as the phosphate when the pH is maintained at 8.5.

5. There is a linear relationship between the initial calcium concentration and the residual magnesium in solution after phosphate precipitation.

6. At higher pH levels only a small amount of calcium precipitates when the initial calcium concentration is low.

7. The recycle of magnesium ammonium phosphate as seed did not increase phosphate recovery at any given pH level.

8. Increasing the retention time during neutralization, digestion and settling did not increase phosphate recovery although it did enhance the precipitation of magnesium.

9. A high ammonium ion concentration, such as that found in digester supernatant, enhances the precipitation of $MgNH_4PO_4 \cdot 6H_2O$ and phosphate recovery. At pH 9.0, a recovery of 96% was obtained. However, the concentration of nitrogen in the precipitated solids decreases with increasing pH above 9.0, thus indicating the precipitation of $Mg_3(PO_4)_2 \cdot 4H_2O$ at the higher pH levels.

10. The precipitation can be carried out continuously (rather than batch-wise) without serious problems in maintaining the systems equilibrium.

## PRECIPITATION BY CHEMICAL ADDITION

All experiments were performed using samples of digester supernatant from the Lake Zurich or Libertyville, Illinois sewage plants. Whenever possible, the same sample of DS was used for individual studies to insure uniformity of raw material. Some experiments were performed using DS from the primary digester. Experiments were performed at a bench and pilot plant scale.

### Bench Scale Experiments

The general procedure used in these experiments is similar to that described in the preliminary precipitation studies. Samples of primary DS from the Libertyville plant containing from 82 to 91 mg/l P as ortho-phosphate were used in these experiments. Five liter samples were treated either with (1) sodium hydroxide alone to raise the pH to the desired level, (2) with a stoichiometric amount of magnesium sulfate followed by ammonium hydroxide or sodium hydroxide for final pH adjustment, or (3) with a stoichiometric amount of magnesia, MgO, followed by sodium hydroxide or

ammonium hydroxide for final pH adjustment. Table III is a summary of the data collected. When MgO (calcined magnesite) is used, final pH of 8.0 may be obtained without addition of a soluble base. The phosphate recovery was only 56% because this type material is not as reactive as the precipitated magnesia. Under similar conditions, when magnesium sulfate is used, a recovery of 76% of phosphate was obtained. At pH 9.0 and 9.5 the phosphate recovery is high even when no magnesium compounds are added. This is due to the fact that DS from the Libertyville Plant contains a high concentration of calcium and magnesium salts. At the higher pH levels, magnesium sulfate plus ammonia gave the lowest residual phosphate. It was observed that liquid solid separation became increasingly difficult with decreases in final pH. A good separation was possible at pH range 9.0-9.5.

Additional experiments were performed using 40% of the stoichiometric amount of magnesia required followed by sodium hydroxide to pH 9.0 and 9.5. Both experiments gave a high degree of phosphate removal similar to that obtained with only sodium hydroxide neutralization.

Table IV shows the data collected when a sample of DS from the secondary digester of the Libertyville sewage treatment plant was used.

The DS tested in these experiments was collected from the mid-point valve of the settler tank of the anaerobic digestion process. During the period when these samples were collected, it was found that practically all the phosphate present in this stream was orthophosphate. Most of the samples of DS contained between 55 and 87 mg/l P. The initial pH of the DS was 7.0.

Three sources of magnesia were used to precipitate the phosphate; (1) solid magnesium oxide (calcined magnesite), (2) precipitated magnesium hydroxide, and (3) precipitated magnesium carbonate. Three levels of magnesia concentration were used because from previous work it had been determined that all the streams from the Libertyville sewage plant contain a surplus of calcium and magnesium ions. Sodium hydroxide or ammonium hydroxide was used for final pH adjustment when the calcined magnesite was used as a source of magnesium ion.

All the experiments were performed using the standard procedure described previously, i.e., 15 minutes for neutralization, 1.0 or 1.5 hours for digestion, and 1 hour settling. The agitation rate was approximately 500 rpm, except for the experiments in which $Mg(OH)_2$ and $MgCO_3$ were used when the agitation was 1,000 rpm. Liquid-solid separation was performed with a batch-type centrifuge. It was observed, qualitatively, that gravity settling could be used if necessary to reduce the volume prior to centrifugation. Solids obtained in experiments where precipitation of phosphate was achieved by the use of ammonia or sodium hydroxide alone were very difficult to settle, prior to centrifugation, or to filter. This type treatment yielded suspensions extremely difficult to handle.

The data in Tables III and IV indicate that similar phosphate recovery could be obtained from the two types of digester supernatant

TABLE III

PRECIPITATION OF PHOSPHATE FROM PRIMARY DIGESTER SUPERNATANT, COLLECTED AT THE LIBERTYVILLE, ILL. SEWAGE TREATMENT PLANT

| Final pH | Chemicals Added | Original P (mg/1) | Residual P (mg/1) | % Recovery P |
|---|---|---|---|---|
| 8.0 | NaOH | 87 | 43 | 50 |
| 8.0 | MgO | 91 | 41 | 56 |
| 8.0 | $MgSO_4$+NaOH | 91 | 22 | 76 |
| 9.0 | NaOH | 87 | 6 | 93 |
| 9.0 | MgO+NaOH | 91 | 3 | 96 |
| 9.0 | $MgSO_4$+NaOH | 91 | 5 | 95 |
| 9.5 | NaOH | 87 | 6 | 93 |
| 9.5 | MgO+NaOH | 81 | 4 | 96 |
| 9.5 | $MgSO_4$+NaOH | 91 | 3 | 97 |
| 9.5 | $MgSO_4$+$NH_4OH$ | 86 | 2 | 98 |
| 9.5 | MgO+$NH_4OH$ | 91 | 3 | 97 |

TABLE IV

PRECIPITATION OF PHOSPHATE FROM SECONDARY DIGESTER SUPERNATANT COLLECTED AT THE LIBERTYVILLE, ILL. SEWAGE TREATMENT PLANT

| Final pH | Chemical Added | Amount $Mg^{++}$ Added(1) | Original P (mg/l) | Residual P (mg/l) | % Recovery P |
|---|---|---|---|---|---|
| 9.0 | MgO+NaOH | 0.2 | 82 | 8 | 90 |
| 9.0 | MgO+NaOH | 0.4 | 82 | 5 | 94 |
| 9.0 | MgO+NaOH | 1.0 | 82 | 5 | 94 |
| 9.0 | $MgO+NH_4OH$ | 0.2 | 82 | 8 | 90 |
| 9.0 | $MgO+NH_4OH$ | 0.4 | 71 | 7 | 90 |
| 9.0 | $MgO+NH_4OH$ | 1.0 | 71 | 5 | 93 |
| 8.9 | $Mg(OH)_2$ | 0.2 | 73 | 6 | 92 |
| 8.9 | $Mg(OH)_2$ | 0.4 | 73 | 6 | 92 |
| 8.9 | $Mg(OH)_2$ | 1.0 | 73 | 6 | 92 |
| 8.7 | $MgCO_3$ | 0.2 | 73 | 10 | 86 |
| 8.7 | $MgCO_3$ | 0.4 | 73 | 8 | 89 |
| 8.7 | $MgCO_3$ | 1.0 | 73 | 7 | 90 |

(1) 1.0 means that a stoichiometric amount of $Mg^{++}$ with respect to P was added.

studied. The final pH adjustment when calcined magnesite is used may be performed with either ammonia or sodium hydroxide. An amount of magnesia less than stoichiometric can be used in this system without greatly affecting the net phosphate removal. Precipitated magnesium hydroxide or magnesium carbonate may be used without final pH adjustment with a soluble base. A slightly higher recovery was observed when the magnesium hydroxide was used.

Four experiments were performed using digester supernatant from the Lake Zurich sewage treatment plant. The sample of DS was obtained from the top of the secondary digester. The objective of these experiments was to determine the pH required for optimum phosphate removal at two temperatures 70°F and 80°F. In these experiments no additional magnesium was added. It was assumed that sufficient cations were present to precipitate the orthophosphate in solution. Either sodium hydroxide or ammonium hydroxide was used as a neutralizing agent. All the experiments were performed using a volume of 5 liters of DS. The neutralization step was performed in approximately 30 minutes. Samples were obtained at pH 8.0, 8.5, 9.0, 9.5 and 10.0. The samples were centrifuged and analyzed for orthophosphate. Figures 5 and 6 show the residual orthophosphate in mg/l P as a function of pH at 70°F and 80°F respectively when sodium hydroxide is used as the neutralizing agent. Figures 7 and 8 show the residual orthophosphate in mg/l P as a function of pH at 70°F and 80°F respectively when ammonium hydroxide is used as the neutralizing agent. In all cases the orthophosphate concentration at the lowest pH represents the concentration present originally in the sample.

When sodium hydroxide is used as a neutralizing agent the lowest residual orthophosphate was obtained at pH 9.0. There is a tendency for the phosphate to go back into solution when the pH is 10.0. When ammonium hydroxide is used as a neutralizing agent the lowest residual concentration of orthophosphate was obtained at pH 10.0 when the experiment was performed at 70°F and pH 9.0 when the experiment was performed at 80°F.

At the optimum pH, a phosphate recovery of 88% was obtained when using either neutralizing agent, i.e., sodium hydroxide or ammonia, at 80°F. At the lower temperature studied, ammonia neutralization at optimum pH, yielded 91% orthophosphate recovery as against 81% for sodium hydroxide. The phosphate recovery under similar experimental conditions, when Libertyville DS was treated with sodium hydroxide is approximately 10% higher than that observed when samples of Lake Zurich DS were used.

## Pilot Plant Studies

Precipitation of phosphate by addition of chemicals was studied at the pilot plant located at the Lake Zurich sewage treatment plant. All these experiments were performed on a batch basis using a volume of digester supernatant ranging from 10 gallons to 40 gallons. In all cases the digester supernatant was transferred on a daily basis

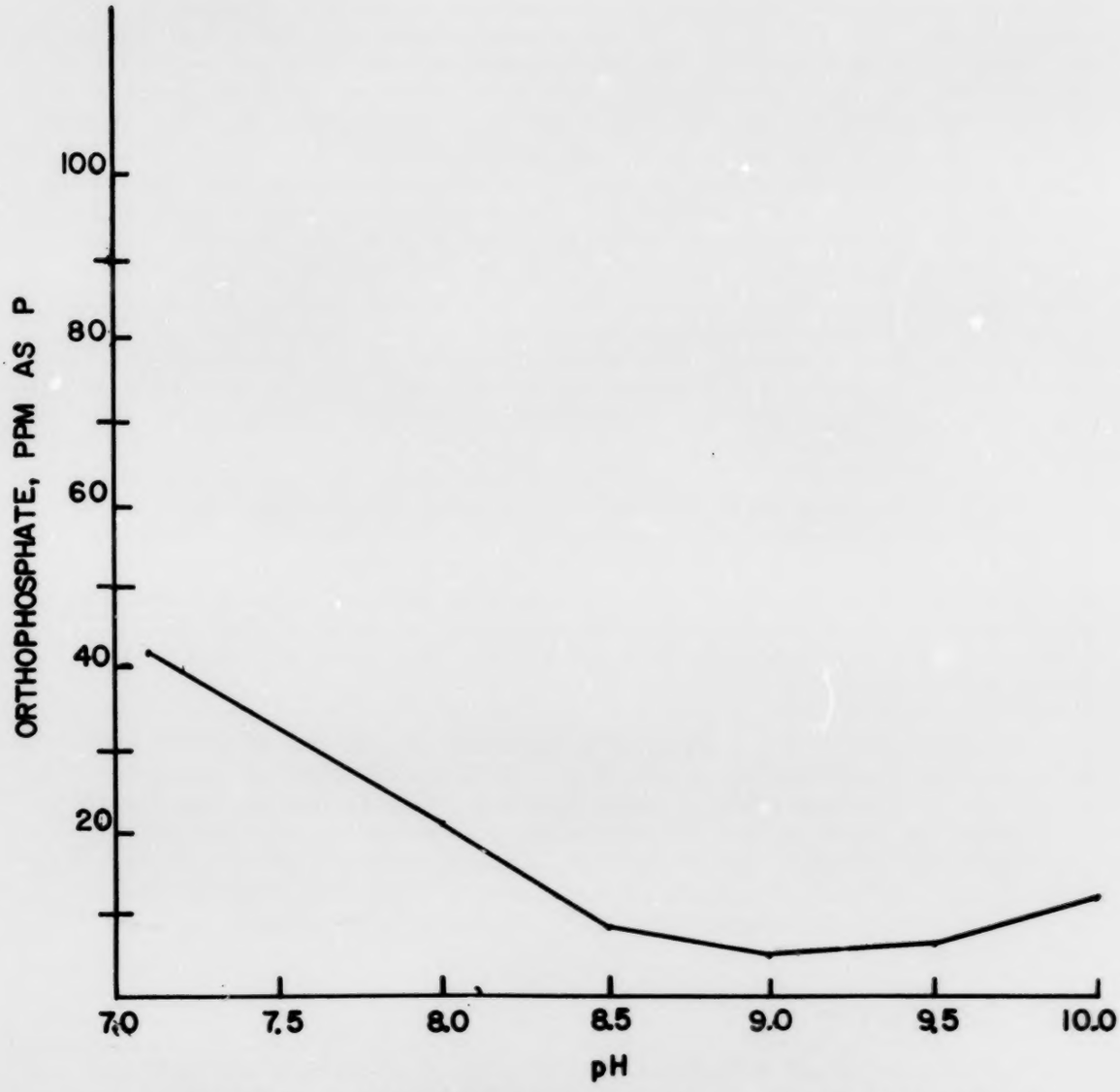



FIGURE 5 RESIDUAL ORTHOPHOSPHATE AS A FUNCTION OF pH. LAKE ZURICH DIGESTER SUPERNATANT TREATED WITH SODIUM HYDROXIDE AT 70° F

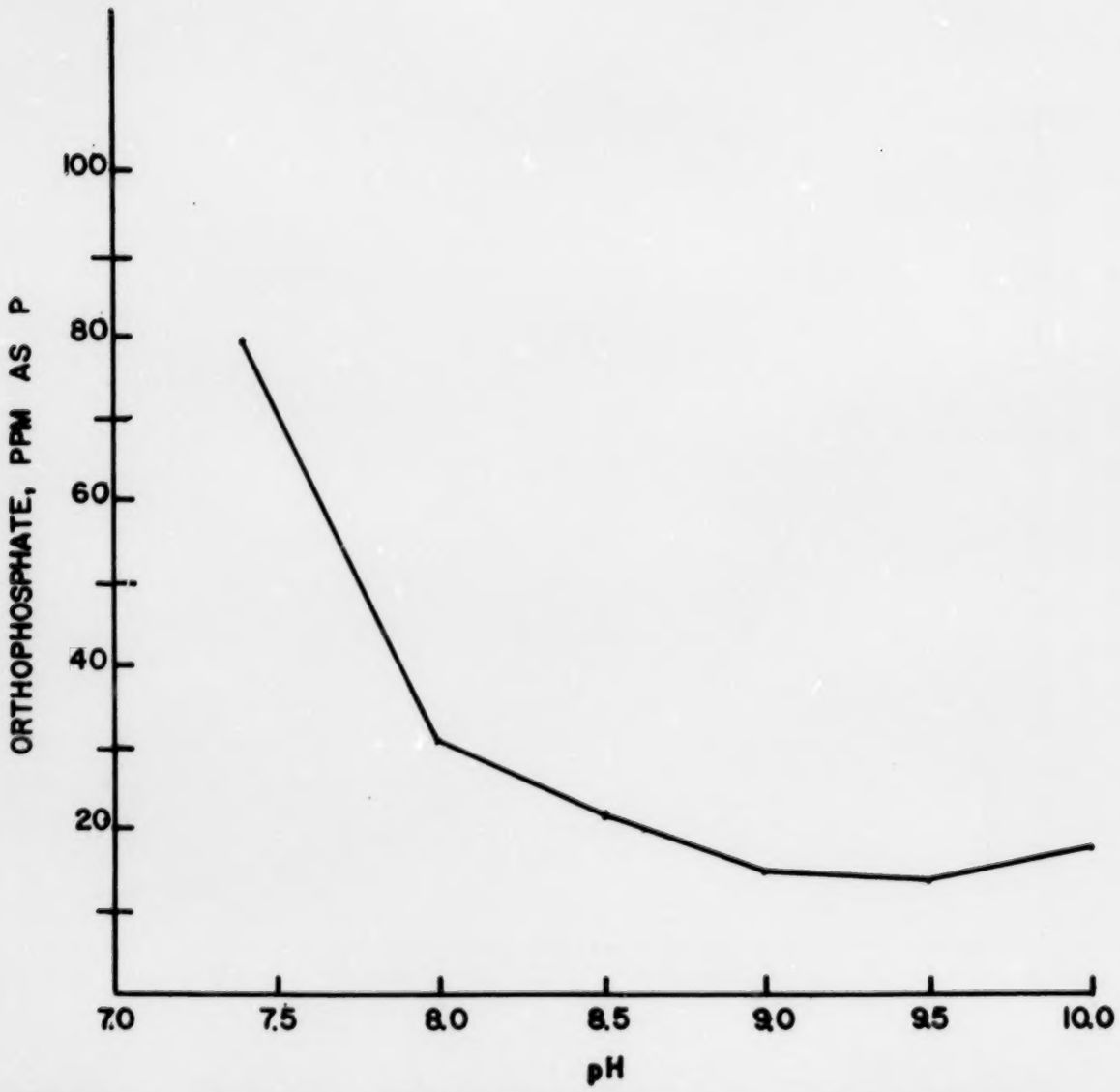



FIGURE 6 RESIDUAL ORTHOPHOSPHATE AS A FUNCTION OF pH. LAKE ZURICH DIGESTER SUPERNATANT TREATED WITH SODIUM HYDROXIDE AT 80° F

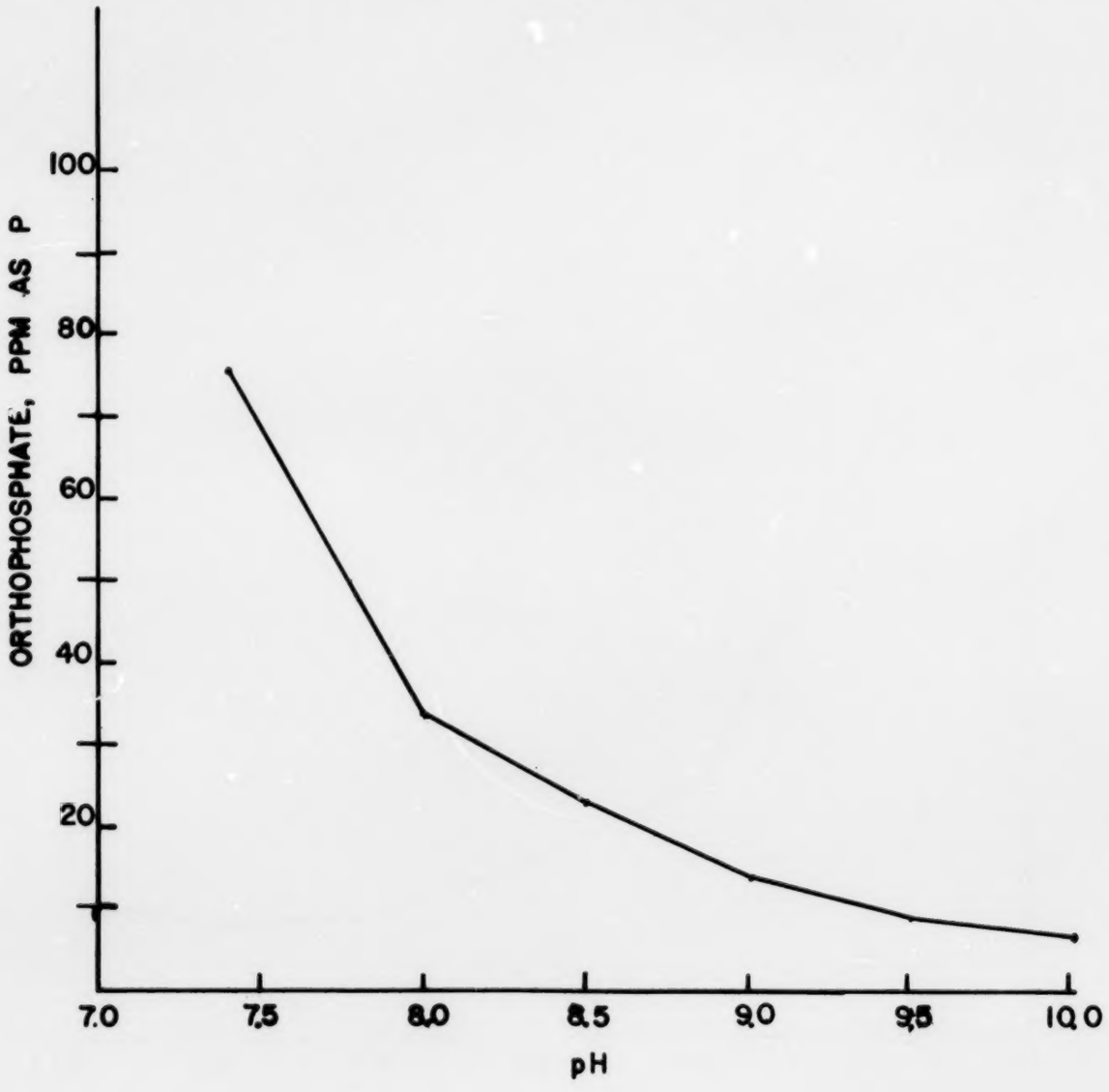



FIGURE 7 RESIDUAL ORTHOPHOSPHATE AS A FUNCTION OF pH LAKE ZURICH DIGESTER SUPERNATANT TREATED WITH AMMONIUM HYDROXIDE AT 70° F

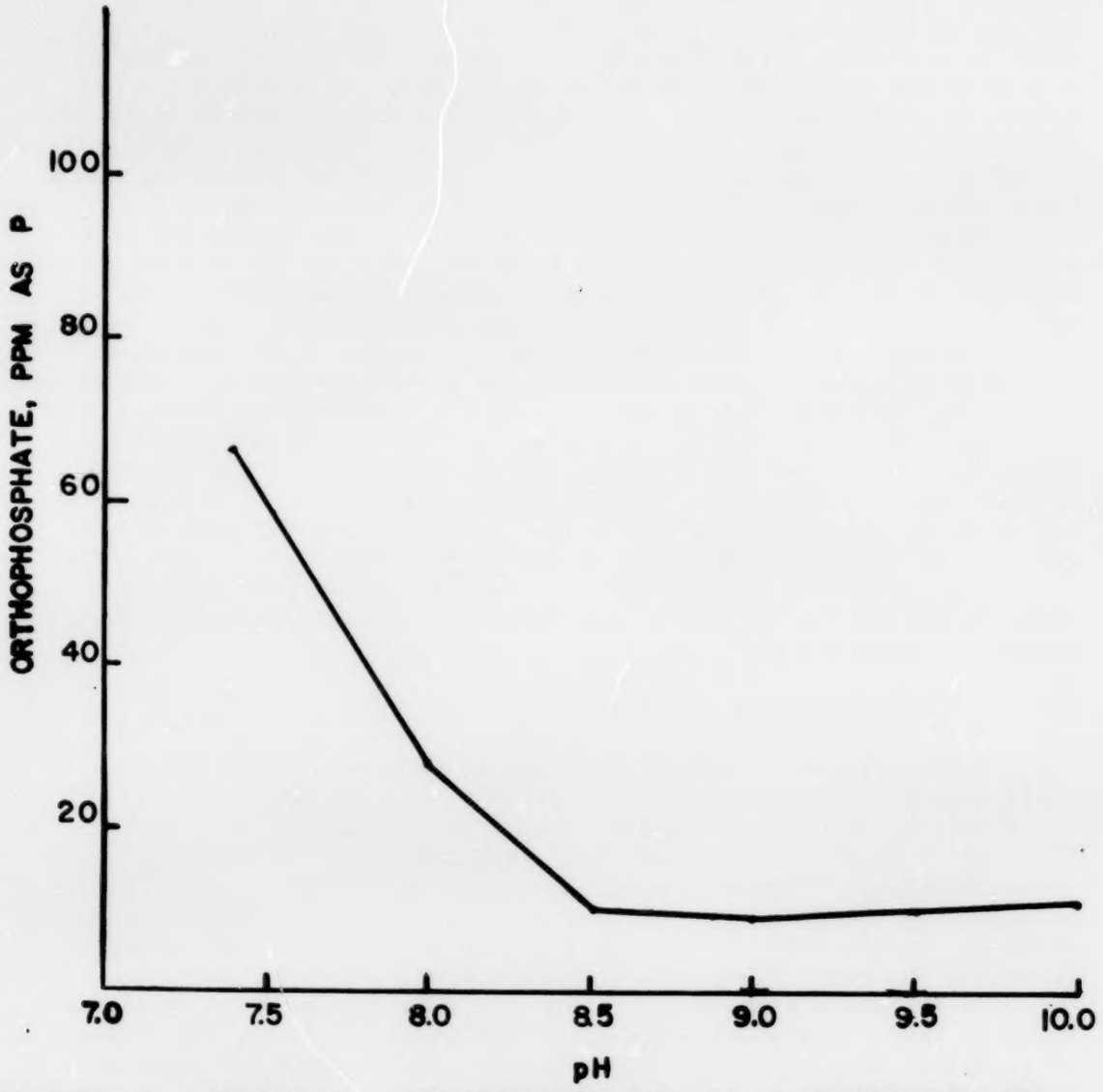



FIGURE 8 RESIDUAL ORTHOPHOSPHATE AS A FUNCTION OF pH. LAKE ZURICH DIGESTER SUPERNATANT TREATED WITH AMMONIUM HYDROXIDE AT 80° F

from the plant's secondary digester to a storage tank of approximately 300 gallons capacity. The storage tank was fitted with a slow moving stirrer to maintain the DS solids in suspension.

The chemicals tested were: (1) magnesium hydroxide (precipitated sea water magnesium hydroxide used as a slurry containing 33% solids), (2) magnesium carbonate (solid $MgCO_3 \cdot 3H_2O$), (3) sodium hydroxide, and (4) ammonium hydroxide.

The procedure used was the same in all cases. A predetermined volume of DS was transferred to a reactor fitted with a stirrer. The chemical treatment used was added either as a solution or a slurry containing approximately 33% solids. The chemical treatment was added in a slug in a few minutes. The treated DS was stirred for approximately two hours. Samples were obtained for analysis after the digestion period. The solid-liquid separation was performed on a batch centrifuge. The data for these experiments is summarized in Table V. The highest phosphate removal was observed when magnesium hydroxide was used in combination with sodium hydroxide at pH 9 or when the magnesium hydroxide was used in combination with a cationic polymer to enhance coagulation. Both experiments indicated a phosphate recovery slightly higher than 90%. Magnesium carbonate at a very low dose, i.e., 35 mg/l as Mg and without need of additional base, yielded a high orthophosphate removal, i.e., 87%. Ammonium hydroxide as a neutralizing agent is more efficient, for phosphate removal, than sodium hydroxide. At 85°F which is the temperature at which the DS is discharged from the secondary digester, the orthophosphate removal was 89%. This is interesting because ammonia is present in the DS and it is a volatile material. This suggests a process whereby ammonia can be used to raise the pH of raw DS to 10.0. Then the precipitated solids containing phosphate are separated from the liquid phase. The treated DS, now free of phosphate and other impurities is flashed under vacuum or air stripped, thus releasing ammonia which is recycled to the incoming raw DS.

## PRECIPITATION BY HEAT DECOMPOSITION

Temperature as a variable was studied using the same operating conditions described on page 16. The DS sample was obtained at Libertyville, Illinois. The experiments were performed at either 50°C, 60°C, or 70°C. Two sources of magnesium ion were studied, precipitated magnesium hydroxide and magnesium carbonate. The levels of magnesium ion concentration used were the same as in the previous section. In all cases, a soluble base was not used and the increase in pH was due only to magnesia neutralization. Table VI summarizes the data for these experiments. From the data in the table it became apparent that temperature had a more pronounced effect on the recovery of phosphate than magnesium stoichiometry and/or source of magnesium ion added. The lowest residual phosphate concentration was obtained at the higher temperature studied. It is also significant that a very high phosphate recovery was achieved at a pH below 9.0.

## TABLE V

### PRECIPITATION OF PHOSPHATE FROM SECONDARY DIGESTER SUPERNATANT PILOT PLANT STUDY AT THE LAKE ZURICH SEWAGE TREATMENT PLANT

| Final pH | Chemical Added | mg/l Added as Mg | Temp. °F | Vol. of Batch (gal.) | pH | Original mg/l | | | | Treated mg/l | | | % Removal | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | TP | OP | COD | SS | TP | OP | COD | TP | OP | COD |
| 8.7 | $Mg(OH)_2$+ NaOH | 70 | 75 | 40 | 7.2 | 93 | 76 | 2580 | 1640 | 16 | 10 | 1416 | 83 | 87 | 45 |
| 9.0 | $Mg(OH)_2$+ NaOH | 70 | 75 | 40 | 7.2 | 93 | 76 | 2580 | 1640 | - | 5 | - | - | 93 | - |
| 7.9 | $Mg(OH)_2$+ NaOH | 50 | 75 | 30 | 7.4 | 63 | 56 | 1660 | - | 20 | - | 864 | 68 | - | 48 |
| 7.9 | $Mg(OH)_2$+ 50 mg/l Polymer(1) | 100 | 75 | 30 | 7.1 | 68 | 56 | 1660 | - | 9 | 5 | 960 | 87 | 91 | 42 |
| 8.7 | $MgCO_3$ | 35 | 80 | 10 | 7.2 | 78 | 69 | 2035 | 1180 | 12 | 9 | 1087 | 85 | 87 | 47 |
| 9.4 | $MgCO_3$ | 35 | 149 | 10 | 7.2 | 78 | 69 | 2035 | 1180 | 13 | 11 | 1122 | 83 | 84 | 45 |
| 9.0 | NaOH | - | 75 | 20 | 7.1 | - | 72 | - | - | 9 | - | - | - | 87 | - |
| 9.0 | NaOH | - | 85 | 10 | 7.1 | 87 | 66 | 2535 | 1680 | 14 | 14 | 1048 | 84 | 79 | 59 |
| 10 | $NH_4OH$ | - | 85 | 10 | 7.0 | 85 | 66 | 2275 | 1103 | 15 | 7 | 1103 | 82 | 89 | 52 |
| 10 | $NH_4OH$ | - | 149 | 10 | 7.2 | 80 | 71 | 1908 | 1360 | 11 | 10 | 937 | 86 | 86 | 51 |

(1) Cationic polyethyleneimine polymer

TP - Total Phosphorus
OP - Orthophosphate Phosphorus
COD - Chemical Oxygen Demand
SS - Suspended Solids

TABLE VI

PRECIPITATION OF PHOSPHATE FROM SETTLED DIGESTER SUPERNATANT WITH MAGNESIA AT HIGH TEMPERATURE

| Reaction Temp. °C | Final pH | Chemical Added | Amount $Mg^{++}$ Added(1) | Original P (mg/l) | Residual P (mg/l) | % Recovery P |
|---|---|---|---|---|---|---|
| 50 | 8.8 | $Mg(OH)_2$ | 0.2 | 73 | 6 | 92 |
| 50 | 8.9 | $Mg(OH)_2$ | 0.4 | 73 | 6 | 92 |
| 50 | 8.8 | $Mg(OH)_2$ | 1.0 | 73 | 6 | 92 |
| 50 | 8.4 | $MgCO_3$ | 0.2 | 71 | 10 | 86 |
| 50 | 9.1 | $MgCO_3$ | 0.4 | 71 | 7 | 90 |
| 50 | 9.2 | $MgCO_3$ | 1.0 | 73 | 6 | 92 |
| 60 | 8.9 | $Mg(OH)_2$ | 0.2 | 73 | 5 | 93 |
| 60 | 8.8 | $Mg(OH)_2$ | 0.4 | 73 | 5 | 93 |
| 60 | 8.9 | $Mg(OH)_2$ | 1.0 | 73 | 4 | 94 |
| 60 | 9.0 | $MgCO_3$ | 0.2 | 71 | 6 | 92 |
| 60 | 8.8 | $MgCO_3$ | 0.4 | 71 | 4 | 94 |
| 60 | 9.1 | $MgCO_3$ | 1.0 | 73 | 6 | 92 |
| 70 | 8.9 | $Mg(OH)_2$ | 0.2 | 73 | 2 | 97 |
| 70 | 8.8 | $Mg(OH)_2$ | 0.4 | 73 | 2 | 97 |
| 70 | 8.8 | $Mg(OH)_2$ | 1.0 | 73 | 3 | 96 |
| 70 | 8.6 | $MgCO_3$ | 0.2 | 71 | 2 | 97 |
| 70 | 8.8 | $MgCO_3$ | 0.4 | 73 | 2 | 97 |
| 70 | 8.8 | $MgCO_3$ | 1.0 | 73 | 2 | 97 |

(1) 1.0 means that a stoichiometric amount of $Mg^{++}$ with respect to P was added.

## Bench Scale Studies

During the evaluation of temperature as a variable, it became apparent that by raising the temperature above 60°C and by using high speed agitation of approximately 1,000 rpm, the pH of the digester supernatant liquor increased without need of adding a neutralizing base. This is due to the decomposition of ammonium bicarbonate, which is present in the liquor, according to the following equation:

$$NH_4HCO_3 \longrightarrow NH_4OH + CO_2$$

It was also found that phosphate would precipitate without the addition of magnesium compounds because the DS used already contains the required cations. In areas where the water is much softer, supplemental magnesium might be required.

Table VII shows the data for experiments performed at 65°C, 70°C and 75°C on a batch process for varied retention periods. The material used in these experiments is secondary settled digester supernatant obtained from the Libertyville sewage treatment plant. The two variables, temperature and retention, are important for maximum phosphate precipitation. It was observed that the best results were obtained when a high rate of agitation was used.

Several experiments were performed using a combination of heat and vacuum to expedite the decomposition of ammonium bicarbonate and thus obtain precipitation of phosphate at a lower operational temperature or a shorter retention time. Again, all these experiments were performed using settled digester supernatant from the Libertyville sewage plant. Table VIII indicates that a substantial amount of phosphate may be precipitated at 40°C when a vacuum of 27" Hg is applied. Practically all the orthophosphate was removed from the system when the temperature was increased to 65°C.

It should be noted that in these experiments the temperature was maintained constant by applying an external source of heat during the specified period of time. The vacuum would lower the initial temperature of the system if heat was not applied.

As mentioned earlier, a high agitation during heating was required to obtain a high level of phosphate removal from the digester supernatant. This means that exposure of a large surface area would expedite evolution of $CO_2$ and thus obtain a high yield of phosphate using shorter retention periods. To verify this hypothesis, experiments were performed using a thin film flash evaporator manufactured by Buchler, Inc. The apparatus can be seen in Figure 9. Samples of digester supernatant from the Libertyville or Lake Zurich plant were introduced into the heating chamber of the flash evaporator. The heating chamber rotates in a constant temperature bath. The experiments were performed using 125 rpm.

## TABLE VII

### PRECIPITATION OF PHOSPHATE BY HEAT TREATMENT FROM SETTLED DIGESTER SUPERNATANT OBTAINED AT THE LIBERTYVILLE PLANT

| Final pH | Temp. °C | Retention Time (Min.) | Original P (mg/l) | Residual P (mg/l) | % Recovery P |
|---|---|---|---|---|---|
| 8.9 | 65 | 60 | 58 | 4 | 94 |
| 8.4 | 65 | 120 | 71 | 2 | 97 |
| 8.4 | 70 | 120 | 71 | 4 | 94 |
| 8.9 | 70 | 180 | 73 | 3 | 95 |
| 8.9 | 75 | 60 | 71 | 3 | 96 |

TABLE VIII

PRECIPITATION OF PHOSPHATE
BY HEAT AND VACUUM FROM
DIGESTER SUPERNATANT OBTAINED
AT THE LIBERTYVILLE PLANT

| Final pH | Temp. °C | Retention Time(Min.) | Original P (mg/l) | Residual P (mg/l) | % Recovery P |
|---|---|---|---|---|---|
| 8.9 | 40 | 60 | 71 | 14 | 80 |
| 8.4 | 40 | 60 | 58 | 9 | 84 |
| 8.5 | 50 | 30 | 71 | 12 | 82 |
| 9.3 | 65 | 60 | 60 | 1 | 98 |
| 9.3 | 65 | 60 | 56 | 1 | 98 |

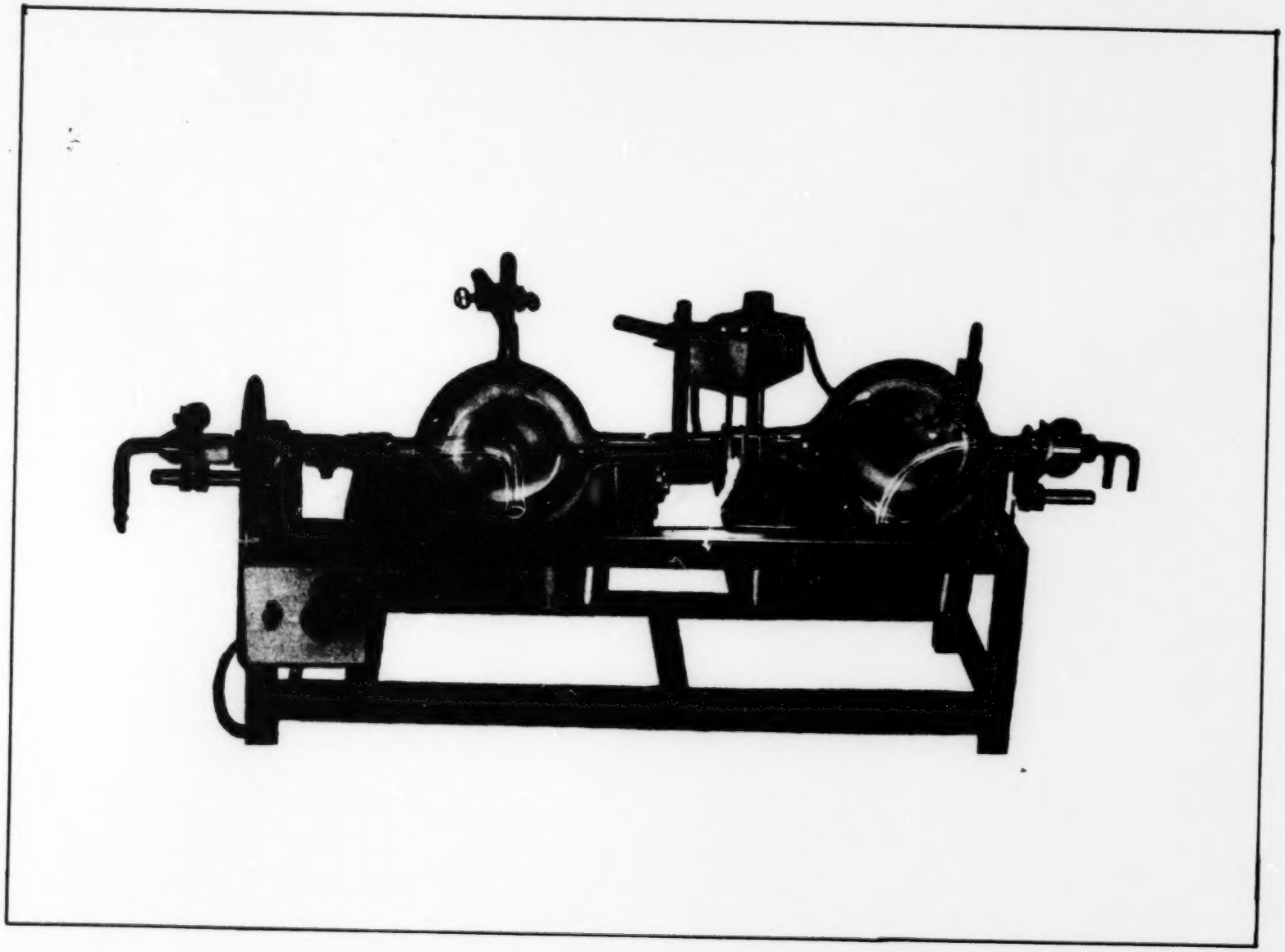


FIGURE 9 FLASH EVAPORATOR APPARATUS

The cooling chamber, which also rotates, collects the evolving gases and also water which evaporates from the heated system. The experimental runs were performed using heat alone or a combination of heat and vacuum. Table IX contains the information on these experiments. In all cases the temperature of the water bath was maintained at 65°C. The operating temperature of the DS inside the heating chamber was not monitored continuously but a spot check indicated a temperature of 60°C. The vacuum was 27" of mercury. After the heat or vacuum and heat treatment period, the entire contents of the flash chamber were transferred into a graduate cylinder to determine any change in volume. When needed, the volume was adjusted to its original level with distilled water. Solid-liquid separation was obtained by centrifugation on a batch basis. The conclusions which may be reached from the information in Table IX are as follows: (1) Heat treatment followed by a period of heat plus vacuum yields a higher phosphate recovery than when the whole period of treatment involves heat plus vacuum. Samples 1 and 4 had a total treatment period of 10 minutes; samples 2 and 6 had a total treatment period of 20 minutes. In both cases the percent recovery of ortho-phosphate is higher when the samples were heated prior to application of a vacuum. (2) Heat alone, for similar pretreatment periods, yields a higher orthophosphate removal than heat plus vacuum; i.e., samples 2 and 8. (3) Longer retention periods increase the orthophosphate recovery yield under all conditions. (4) Orthophosphate precipitation in a thin film flash evaporator is not substantially higher than when the experiments are performed in a vessel with high speed agitation. (5) Percent nitrogen removal was substantially higher when a short period of heat plus vacuum was used after a period of heating the DS; i.e., experiments 6, 7 and 8.

To understand the relationship between $CO_2$ and volatile nitrogen evolution (probably as ammonia), a series of experiments were performed using a synthetic solution of ammonium bicarbonate in distilled water. The concentration of ammonium bicarbonate was similar to that present in the digester supernatant of Libertyville. All the experiments were performed in the flash evaporator following the procedure outlined in the previous section. Figure 10 shows the rate at which $CO_2$ and N are removed from the liquid phase as a function of time, when only heat is applied to the system. Figure 11 shows the rate at which $CO_2$ and N are removed from the liquid phase when heat and vacuum are applied. From the information in Figures 10 and 11 it becomes clear that heat alone encourages a faster evolution of $CO_2$ than ammonia. Under heat and vacuum the $CO_2$ evolves at a higher but parallel rate with ammonia. An evaluation of the pH behavior for the two systems indicates that the pH goes up as a function of time when heat alone is used and it decreases as a function of time in the heat-vacuum system. These experiments suggest that the precipitation of orthophosphate from DS should be more efficient if performed in two steps. The DS should first be heated under high agitation and then the heated DS treated under heat and a slight vacuum in a separate reactor.

The phosphate precipitation process by heat decomposition was also tested in a continuous system. A four liter reactor fitted with a high speed agitator and a heating mantle was used. The DS was pumped continuously at a rate calculated to give a 2-hour retention time.

TABLE IX

PRECIPITATION OF PHOSPHATE BY HEAT & VACUUM
IN A THIN FILM FLASH EVAPORATOR

| Sample No. | Source of Sample | Heat Treatment Time (Min.) | Heat & Vacuum Treatment Time (Min.) | % Removal | | pH | |
|---|---|---|---|---|---|---|---|
| | | | | OP | TN | Original | Final |
| 1 | Libertyville | 0 | 10 | 69 | - | 7.3 | 8.4 |
| 2 | Libertyville | 0 | 20 | 73 | - | 7.2 | 8.2 |
| 3 | Libertyville | 0 | 30 | 91 | - | 7.2 | 8.2 |
| 4 | Libertyville | 5 | 5 | 74 | - | 7.4 | 8.3 |
| 5 | Libertyville | 10 | 5 | 84 | - | 7.4 | 8.4 |
| 6 | Libertyville | 15 | 5 | 85 | 44 | 7.3 | 8.6 |
| 7 | Lake Zurich | 15 | 5 | 85 | 42 | 7.0 | 8.5 |
| 8 | Libertyville | 20 | 0 | 81 | 12 | 7.2 | 8.9 |

OP - Orthophosphate Phosphorus
TN - Total Nitrogen

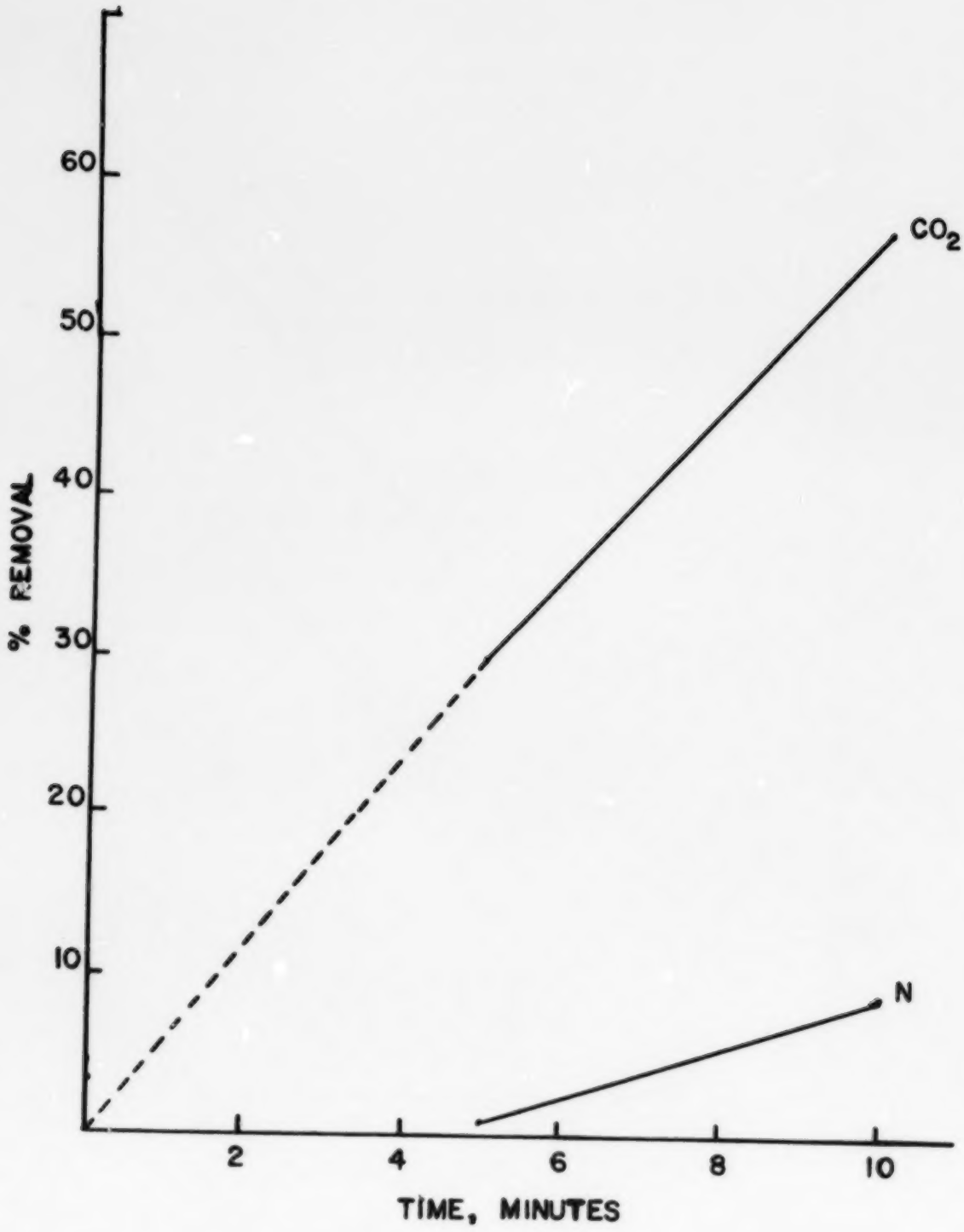



FIGURE 10 CARBON DIOXIDE AND NITROGEN REMOVAL AS A FUNCTION OF TIME AT 65° C

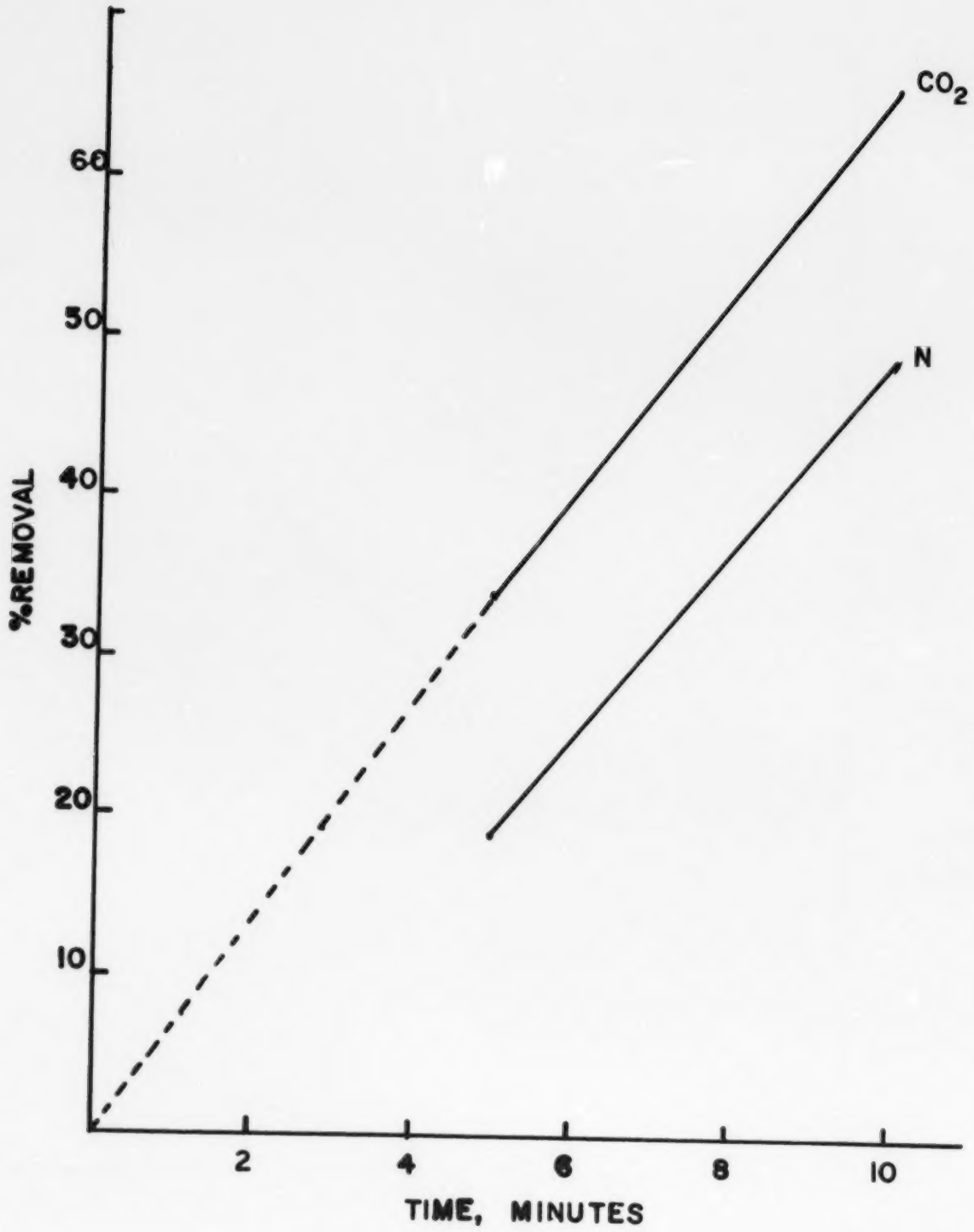



FIGURE II CARBON DIOXIDE AND NITROGEN REMOVAL AS A FUNCTION OF TIME AT 65°C AND A VACUUM OF 27" OF MERCURY

Two continuous runs were performed, one at 70°C and the other at 65°C. The percent recovery of phosphate averaged 90% and 87% respectively. It was difficult to maintain a steady temperature because the heater control was not adequate. These two experiments were performed with digester supernatant from the Libertyville sewage treatment plant.

## Pilot Plant Studies

To verify the results obtained with bench scale laboratory equipment, and in most cases, performed with DS from the Libertyville sewage treatment plant; larger scale pilot plant studies were performed using digester supernatant from the Lake Zurich sewage treatment plant.

Figure 12 shows the schematic of the equipment used in the pilot plant studies. In Figure 13 can be seen a photograph of the pilot plant mounted in a trailer at the Lake Zurich sewage treatment plant location. Figure 14 shows a close up of the reactor, the storage tanks and the flashing chamber.

Batch Experiments. All these experiments were performed in a reactor of 30 gallon capacity manufactured by Groen, Inc. The reactor has a double jacket which contains water that can be heated by a sealed electrical element. Temperature can be accurately controlled by a built-in thermostat which allows variation of $\pm$ 2°C. The digester supernatant was transferred on a daily basis from the sewage treatment plant's secondary digester to the pilot plant storage tank which can hold up to 300 gallons. The digester supernatant was maintained under slight agitation to ensure a uniform raw material. A centrifugal pump was used to transfer DS from the storage tank to the reactor. The reactor was fitted with a lightning mixer with a motor of 1/12 hp. The stirrer was capable of operation at 1700 rpm. A centrifugal pump was used to discharge from the reactor. The rate of discharge could be adjusted with a gate valve located in front of the pump. Samples of DS heated with and without agitation were collected at several time intervals. The samples were centrifuged in a batch centrifuge for approximately 10 minutes. The liquid phase was analyzed for residual orthophosphate, $CO_2$, N and COD.

The effect of agitation on the precipitation of phosphate from digester supernatant was studied at 65°C. In Figure 15 can be seen the residual orthophosphate in mg/l P as a function of time for experiments with and without stirring at 65°C. Obviously stirring does play an important role in the precipitation of orthophosphate. Table X summarizes the data on pH, residual $CO_2$, N and COD. Evaluation of the $CO_2$ residual and pH behavior explains the higher phosphate recovery when agitation is used; i.e., a higher pH which means a lower carbon dioxide concentration, decreases the solubility of phosphate compounds and thus a higher orthophosphate recovery is possible. Nitrogen concentration decreased by approximately 80 mg/l and 60 mg/l respectively after 30 minutes when stirring and heat alone were used.

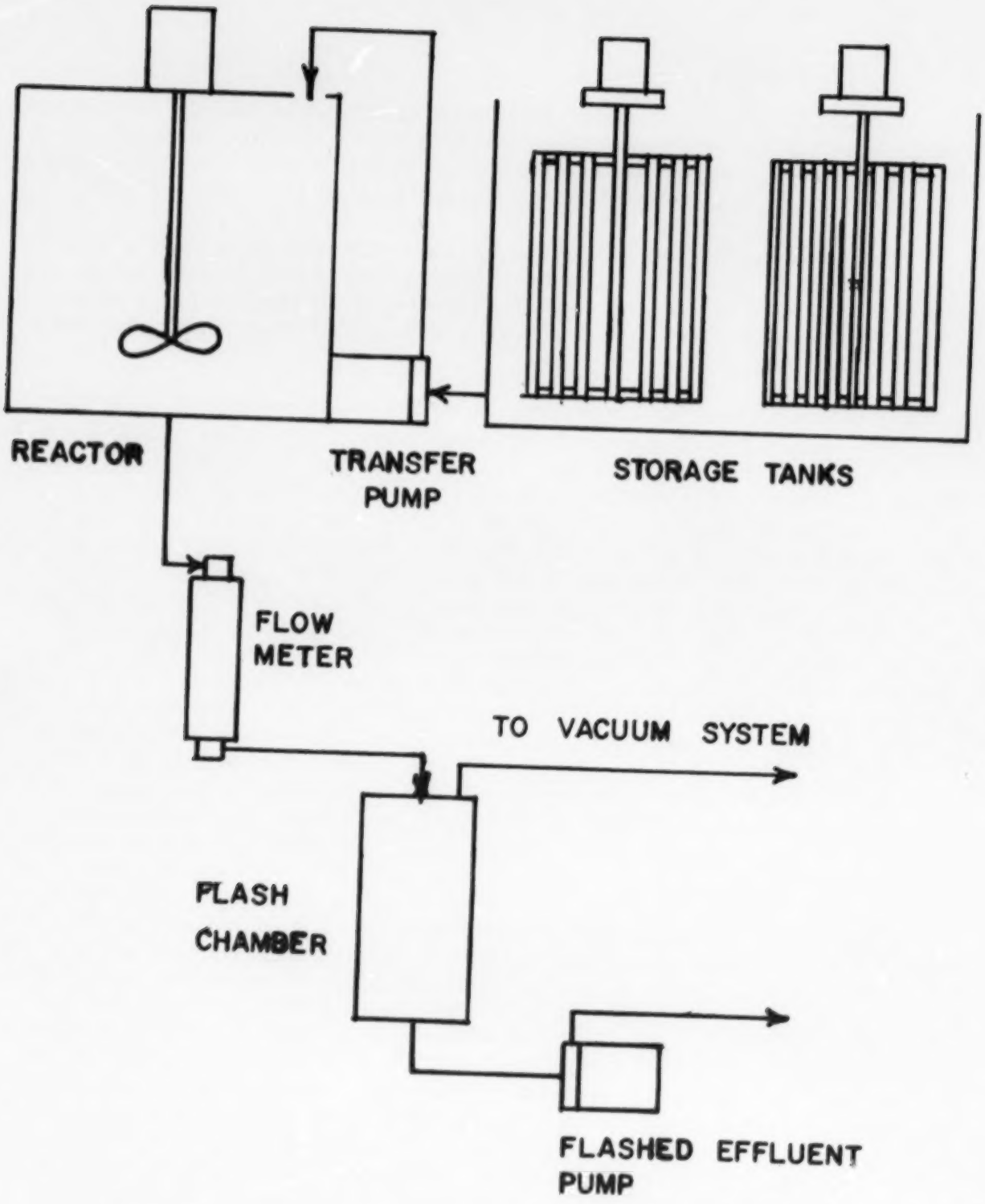



FIGURE 12 SCHEMATIC OF THE PILOT PLANT EQUIPMENT

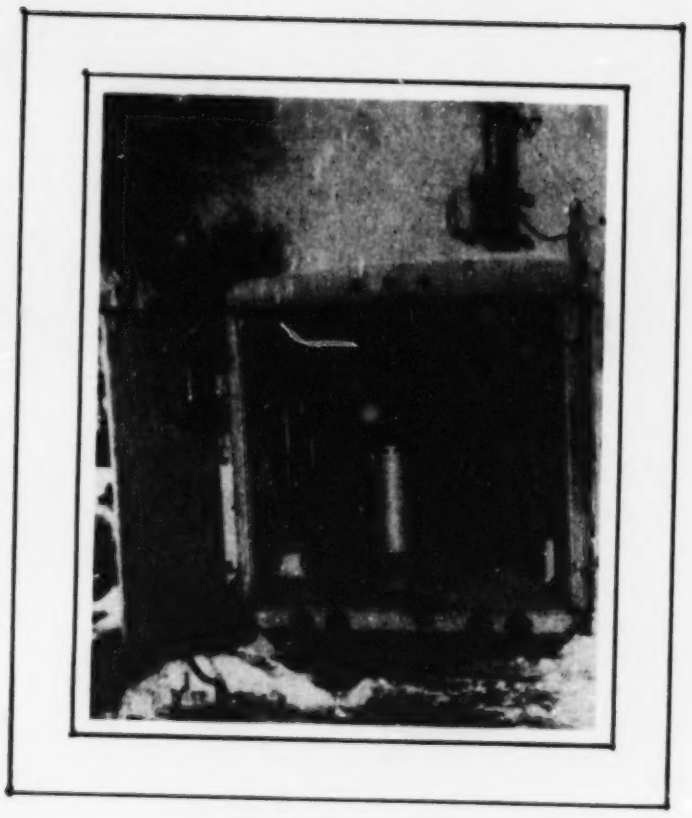
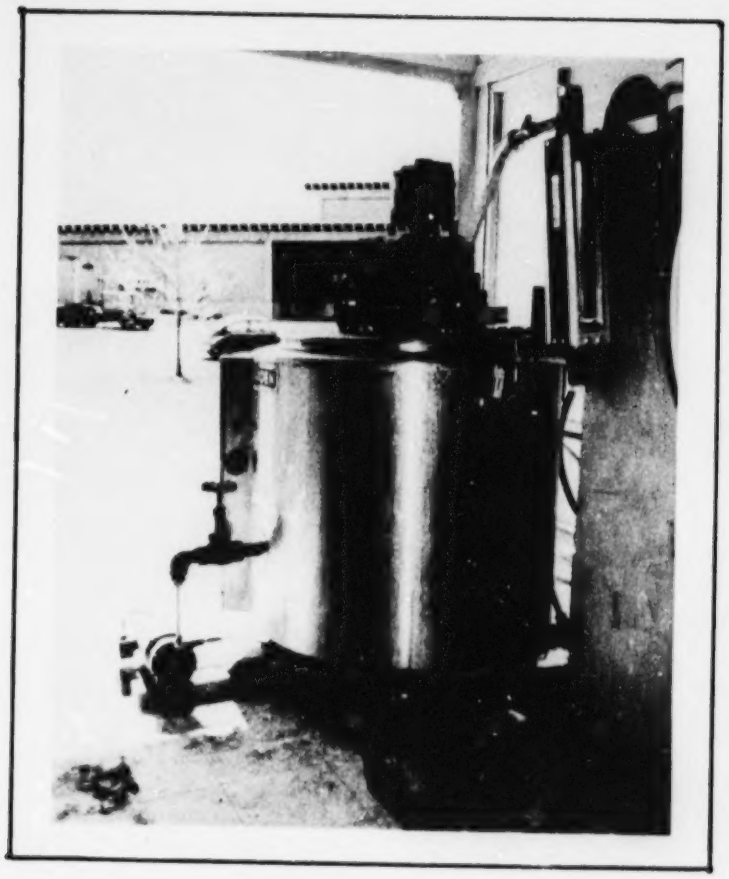
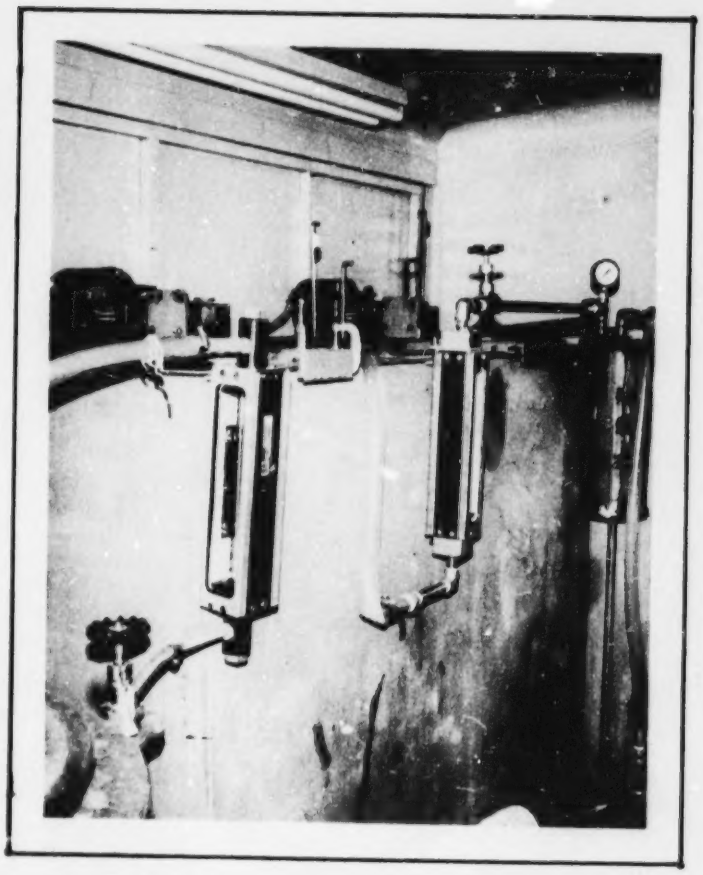


FIGURE 13 PHOTOGRAPH OF THE PILOT PLANT TRAILER





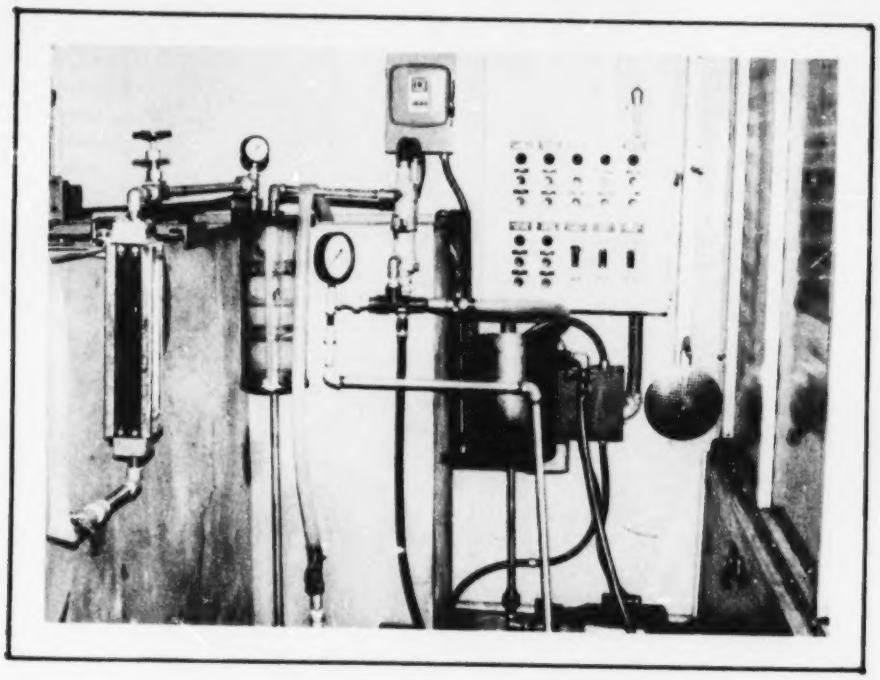


FIGURE 14 PHOTOGRAPH OF THE REACTOR, STORAGE TANKS, AND FLASHING CHAMBER

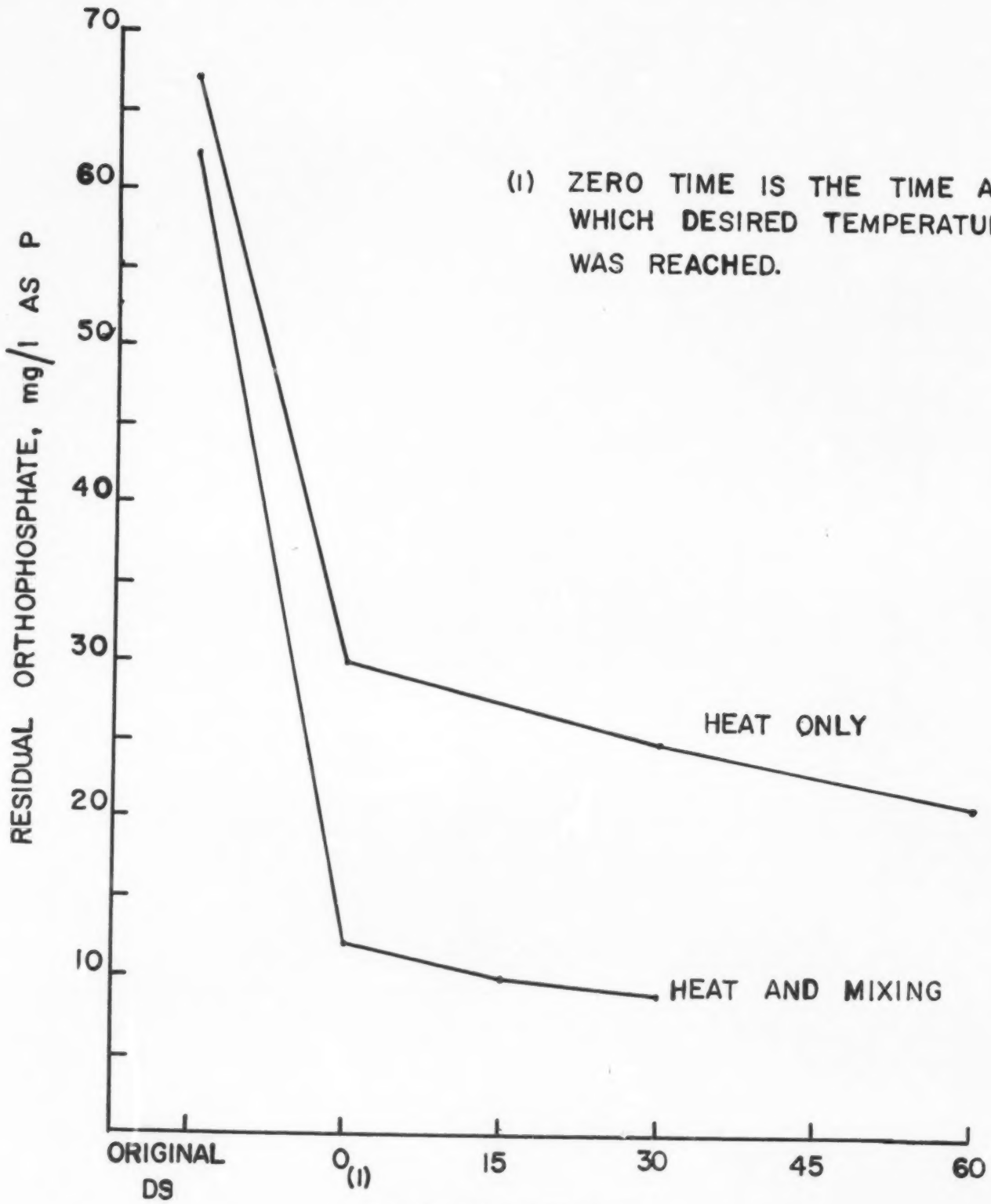



FIGURE 15 THE EFFECT OF AGITATION ON PRECIPITATION OF ORTHOPHOSPHATE FROM DIGESTER SUPERNATANT BY HEAT TREATMENT AT 65° C

TABLE X

RESIDUAL CARBON DIOXIDE, COD AND TOTAL NITROGEN IN DIGESTER SUPERNATANT HEATED AT 65°C WITH AND WITHOUT STIRRING

| Concentration mg/l | Heat Only | | | | Heat and Stirring | | | |
|---|---|---|---|---|---|---|---|---|
| | Original | 0 Time (1) | 15 min | 30 min | Original | 0 Time (1) | 15 min | 30 min |
| $CO_2$ | 2156 | 1980 | 1980 | 1936 | 1980 | 1768 | 1108 | 915 |
| COD | 1782 | 1686 | 1004 | 875 | 1700 | 976 | 968 | 772 |
| TKN | 626 | 615 | 583 | 563 | 604 | 551 | 537 | 518 |
| pH | 7.0 | 7.5 | 7.9 | 7.9 | 7.6 | 8.9 | 9.3 | 9.3 |

(1) Time at which temperature was reached.

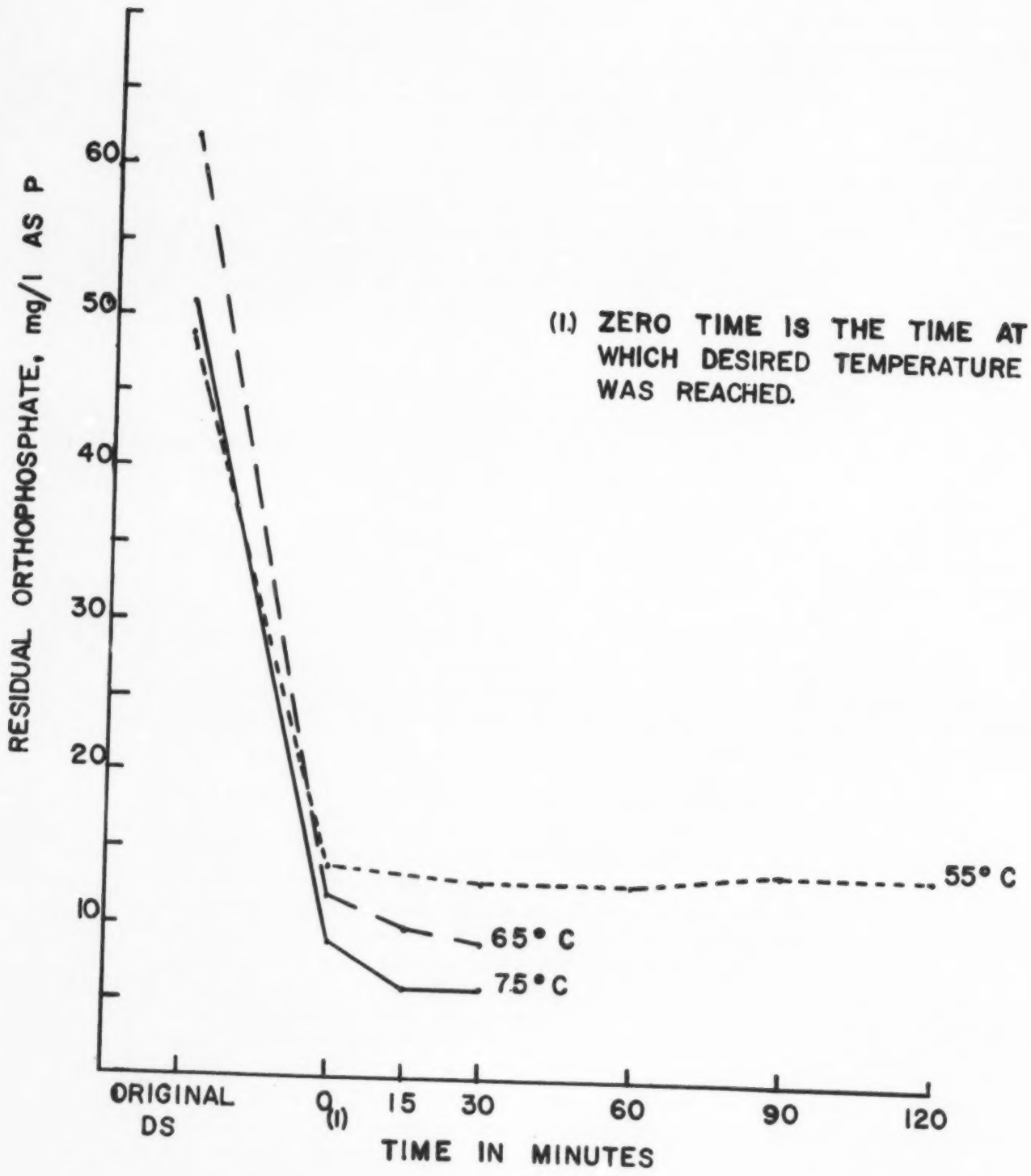
COD - Chemical Oxygen Demand
TKN - Total Kjeldahl Nitrogen

A series of batch experiments were designed to study the effect of temperature and retention time on the precipitation of orthophosphate from digester supernatant by heat. All the experiments were performed under the same conditions. A volume of approximately 14 gallons of digester supernatant was transferred to the reactor. The stirrer was set at 1700 rpm and the temperature was raised to reach the desired level. Usually, approximately 15 minutes was required to reach equilibrium. Samples were taken at predetermined time intervals. The samples were centrifuged in a batch type centrifuge and analyzed for orthophosphate. Three temperature levels were studied 56°C, 65°C, and 75°C. Figure 16 shows the residual orthophosphate for each temperature as a function of time. A residual orthophosphate below 10 mg/l P was obtained at either 65°C or 75°C regardless of the retention time. The residual orthophosphate was higher than 10 mg/l P and remained fairly constant up to 2 hours when the temperature was 55°C. In all cases the highest reduction of orthophosphate was observed during the first 15 minutes of heating from the original temperature of the DS to the desired temperature.

Continuous Experiments. During the preliminary work, all the equipment was calibrated and the reactor was tested under varied operating conditions. Some difficulty was experienced with the flow meters and the centrifugal pumps. In both cases, when operating at low flows, there was a tendency to plug with the suspended solids present in the digester supernatant. This type problem should not be present when operating with larger size equipment since the suspended solids present in the digester supernatant have very small particle sizes.

A total of twenty seven continuous runs were performed. Equilibrium in the system was reached quickly because of the size of equipment and type of operation. The length of the continuous runs was from 2 to 6 hours. Retention time varied from 15 to 120 minutes. The temperatures studied were 65, 70, 75 and 80°C.

The operation in all cases was similar. Digester supernatant was collected on a daily basis from the secondary digester of the Lake Zurich sewage treatment plant. The digester supernatant was stored in a tank which can hold up to 300 gallons. The digester supernatant was constantly stirred at a very low rate to ensure uniformity. A predetermined volume of DS was transferred to the reactor where it was heated up to the desired temperature. A stirrer set at 1700 rpm was used during the operation. Once the temperature desired was reached, digester supernatant from the storage vessel was continuously pumped into the reactor at a predetermined rate. The flow was regulated by a gate or needle valve depending on the flow desired. The flow was monitored on a regular time basis. A flow meter was installed between the pump and the reactor. The incoming steam was directed through a pipe to the wall of the reactor opposite to the outlet pipe to minimize by-passing. The treated DS was pumped out of the reactor into a 40 gallon drum which was calibrated. The volume




(1) ZERO TIME IS THE TIME AT WHICH DESIRED TEMPERATURE WAS REACHED.

FIGURE 16 THE EFFECT OF TEMPERATURE AND RETENTION TIME ON ORTHOPHOSPHATE REMOVAL FROM DS

of DS received from the reactor was monitored on a time basis. Hourly spot samples were collected and centrifuged in a batch centrifuge for analysis.

In Table XI can be seen the data for runs at 65°C. The conclusions which may be drawn from the data are as follows:

1. Orthophosphate may be precipitated without addition of chemicals from DS in a continuous process.

2. An average of 80% removal may be obtained at 65°C when the retention time is held from 45 to 60 minutes.

3. A removal of 80-90% orthophosphate is possible at a retention higher than 90 minutes.

4. Digester supernatant from the Lake Zurich and the Libertyville plants behave equally under similar operating conditions.

5. The removal of total phosphate parallels the behavior observed for the soluble orthophosphate. In general cations do not precipitate non-orthophosphate P and therefore differences may occur when a large amount of soluble non-orthophosphate P is present in the DS.

6. A substantial amount of COD is removed by the heat treatment of DS. On the average a 50% removal can be anticipated under these operating conditions.

Information on the continuous runs performed at 70°C is summarized in Table XII. A shorter retention time than that used at 65°C was studied. Two runs with a 15 minute retention time verified that the reactor was too small to reach equilibrium when 1 gallon per minute was continuously pumped into the reactor with a volume of 15 gallons. In both cases the residual orthophosphate of 10 mg/l obtained in the first two samples increased to 16 mg/l as a function of time. In both cases the first two samples were taken in 15 minute intervals; the other samples were taken after 1 hour and 2 hour operation. The residual $CO_2$ is also low in the first two samples but then increases in the latter part of the experiment.

A 30 minute retention time yielded an 80% removal of orthophosphate and total phosphate. Again, the percent COD removed was close to 50%.

Table XIII contains the data for continuous runs performed at 75°C. These results indicate that at 75°C a removal of 85% to 90% of the orthophosphate may be expected. The percent removal of total phosphate was also in the same range. The COD removal was slightly higher than the previous 50% average obtained at the lower temperatures. It appears that a longer retention time does not improve the percent removal of any of the impurities. This may be due to variations in the characteristics of the digester supernatant which was used in the different experiments.

TABLE XI

PRECIPITATION OF PHOSPHATE FROM DIGESTER SUPERNATANT BY HEAT TREATMENT - 65°C CONTINUOUS RUNS

(LAKE ZURICH SEWAGE TREATMENT PLANT)

| Exp. No. | Volume in Reactor(gal) | Retention Time(min) | Original | | | | | | Treated | | | | | % Removal | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | pH | OP | TP | $CO_2$ (mg/l) | COD | SS | pH | OP | TP | $CO_2$ (mg/l) | COD | OP | TP | $CO_2$ | COD |
| 1 | 16 | 45 | 7.2 | 71 | 85 | 2200 | 2166 | - | 8.5 | 18 | 21 | 1900 | 1150 | 75 | 75 | 14 | 47 |
| | | | | | | | | | 8.5 | 17 | 19 | 1800 | 1190 | 76 | 78 | 18 | 45 |
| | | | | | | | | | 8.5 | 17 | 20 | 1870 | 1190 | 76 | 76 | 15 | 45 |
| | | | | | | | | | 8.6 | 15 | 18 | 1730 | 1160 | 79 | 79 | 21 | 46 |
| | | | | | | | | | 8.6 | 12 | 18 | 1720 | 1140 | 83 | 79 | 22 | 47 |
| | | | | | | | | | 8.7 | 14 | 19 | 1640 | 1120 | 80 | 78 | 25 | 48 |
| | | | | | | | | | 8.7 | 12 | 18 | 1660 | 1150 | 83 | 79 | 24 | 47 |
| 2(1) | 10 | 60 | 7.2 | 64 | 67 | - | 1930 | 480 | 8.7 | 8 | 11 | - | 700 | 87 | 84 | - | 64 |
| | | | | | | | | | 9.5 | 12 | 16 | - | 1050 | 81 | 76 | - | 45 |
| | | | | | | | | | 9.0 | 14 | 17 | - | 1070 | 78 | 75 | - | 44 |
| | | | | | | | | | 8.9 | 13 | 16 | - | 1030 | 80 | 76 | - | 47 |
| | | | | | | | | | 9.1 | 12 | 14 | - | 870 | 81 | 79 | - | 55 |
| 3 | 16 | 60 | 7.2 | 78 | 103 | 2700 | 2850 | 2240 | - | 15 | 16 | 1800 | 1360 | 81 | 84 | 33 | 52 |
| | | | | | | | | | | 14 | 15 | - | 1280 | 82 | 85 | - | 55 |
| 4 | 18 | 90 | 7.2 | 67 | 69 | 2217 | 2790 | 1980 | 8.5 | 9 | 18 | 1840 | 1210 | 87 | 74 | 17 | 56 |
| | | | | | | | | | 8.8 | 9 | 16 | 1630 | 1350 | 87 | 77 | 26 | 51 |
| | | | | | | | | | 8.8 | 8 | 14 | 1500 | 1370 | 88 | 80 | 32 | 51 |
| | | | | | | | | | 8.9 | 9 | 14 | 1440 | 1380 | 87 | 80 | 35 | 50 |
| | | | | | | | | | 8.8 | 7 | 13 | 1500 | 1350 | 90 | 81 | 32 | 53 |
| 5 | 16 | 120 | 7.1 | 71 | - | - | - | - | 8.6 | 11 | - | - | - | 85 | - | - | - |
| | | | | | | | | | 9.0 | 9 | - | - | - | 87 | - | - | - |
| | | | | | | | | | 9.1 | 9 | - | - | - | 87 | - | - | - |
| | | | | | | | | | 9.1 | 8 | - | - | - | 89 | - | - | - |
| | | | | | | | | | 9.2 | 8 | - | - | - | 89 | - | - | - |
| | | | | | | | | | 9.2 | 8 | - | - | - | 90 | - | - | - |

(1) Sample from the Libertyville Waste Treatment Plant

OP - Orthophosphate Phosphorus
TP - Total Phosphorus
COD - Chemical Oxygen Demand
SS - Suspended Solids

TABLE XII

PRECIPITATION OF PHOSPHATE FROM DIGESTER SUPERNATANT BY HEAT TREATMENT - 70°C CONTINUOUS RUNS
(LAKE ZURICH SEWAGE TREATMENT PLANT)

| Exp. No. | Volume in Reactor(gal) | Retention Time(min) | Original | | | | | Treated | | | | | % Removal | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | pH | OP | TP | $CO_2$ (mg/1) | COD | pH | OP | TP | $CO_2$ (mg/1) | COD | OP | TP | $CO_2$ | COD |
| 1 | 15 | 15 | 7.1 | 64 | - | 2190 | - | 8.9 | 10 | - | 1460 | - | 84 | - | 33 | - |
| | | | | | | | | 8.9 | 10 | - | 1340 | - | 84 | - | 39 | - |
| | | | | | | | | 8.5 | 16 | - | 1790 | - | 75 | - | 18 | - |
| | | | | | | | | 8.4 | 16 | - | 1812 | - | 75 | - | 17 | - |
| 2 | 15 | 15 | 7.1 | 62 | - | 2190 | - | 8.9 | 10 | - | 1460 | - | 84 | - | 33 | - |
| | | | | | | | | 8.9 | 10 | - | 1340 | - | 84 | - | 39 | - |
| | | | | | | | | 8.5 | 16 | - | 1790 | - | 74 | - | 18 | - |
| | | | | | | | | 8.5 | 16 | - | 1812 | - | 74 | - | 17 | - |
| 3 | 13 | 30 | 7.4 | 54 | 53 | 2112 | 1930 | 8.7 | 14 | 13 | 1640 | 1030 | 74 | 75 | 22 | 47 |
| | | | | | | | | 8.8 | 9 | 11 | 1340 | 1020 | 81 | 79 | 35 | 47 |
| | | | | | | | | 8.6 | 11 | 10 | 1610 | 1020 | 80 | 81 | 24 | 47 |

OP - Orthophosphate Phosphorus
TP - Total Phosphorus
COD - Chemical Oxygen Demand
SS - Suspended Solids

## TABLE XIII

PRECIPITATION OF PHOSPHATE FROM DIGESTER SUPERNATANT BY HEAT TREATMENT - 75°C CONTINUOUS RUNS
(LAKE ZURICH SEWAGE TREATMENT PLANT)

| Exp. No. | Volume in Reactor(gal) | Retention Time(min) | Original | | | | | | Treated | | | | | % Removal | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | pH | OP | TP | $CO_2$ | COD | SS | pH | OP | TP | $CO_2$ | COD | OP | TP | $CO_2$ | COD |
| | | | | | | (mg/l) | | | | | (mg/l) | | | | | | |
| 1 | 8 | 15 | 7.2 | 62 | 102 | 2200 | 2340 | 1700 | 9.0 | 9 | 12 | 1280 | 1070 | 85 | 88 | 42 | 54 |
| | | | | | | | | | 8.9 | 8 | 13 | 1320 | 1100 | 87 | 87 | 40 | 53 |
| | | | | | | | | | 8.9 | 9 | 10 | 1460 | 1090 | 85 | 90 | 33 | 53 |
| | | | | | | | | | 8.8 | 10 | 12 | 1510 | 1060 | 84 | 88 | 31 | 55 |
| | | | | | | | | | 8.9 | 9 | 9 | 1440 | 1010 | 85 | 91 | 34 | 57 |
| | | | | | | | | | 9.5 | 5 | 7 | - | 1010 | 90 | 93 | - | 57 |
| | | | | | | | | | 8.9 | 8 | 9 | 1350 | 1010 | 87 | 91 | 38 | 57 |
| 2 | 15 | 30 | 7.2 | 61 | 92 | 2200 | 2068 | 1100 | 8.7 | 9 | 14 | 1190 | 1150 | 85 | 85 | 28 | 49 |
| | | | | | | | | | 8.7 | 8 | 13 | 1510 | 1050 | 87 | 86 | 31 | 49 |
| | | | | | | | | | 8.5 | 10 | 14 | 1740 | 1050 | 84 | 85 | 21 | 49 |
| | | | | | | | | | 8.5 | 11 | 14 | 1810 | 1070 | 82 | 85 | 18 | 48 |
| | | | | | | | | | 8.8 | 7 | 11 | 1450 | 1010 | 89 | 88 | 34 | 51 |
| | | | | | | | | | 8.9 | 8 | 11 | 1370 | 1010 | 87 | 88 | 38 | 51 |
| | | | | | | | | | 9.0 | 7 | 11 | 1300 | 990 | 89 | 88 | 41 | 52 |
| 3 | 15 | 45 | 7.1 | 63 | 80 | 2217 | 1990 | - | 9.0 | 9 | 12 | 1090 | 1130 | 86 | 85 | 51 | 43 |
| | | | | | | | | | 8.8 | 9 | 11 | 1450 | 1080 | 86 | 86 | 35 | 45 |
| | | | | | | | | | 8.8 | 9 | 11 | 1480 | 1070 | 86 | 86 | 33 | 46 |

OP - Orthophosphate Phosphorus
TP - Total Phosphorus
COD - Chemical Oxygen Demand
SS - Suspended Solids

The last group of continuous experiments was performed at 80°C to determine if a higher operating temperature could decrease the solublity of the phosphates which precipitate from digester supernatant without addition of chemicals. Table XIV summarizes the data for these experiments.

At 80°C it appears that the lower retention time of 15 minutes is optimum. Therefore, at the higher temperatures, higher retention is not recommended. The residual orthophosphate found in the experiment using Libertyville DS is similar to that obtained with the Lake Zurich material, but the calculated percent recoveries are lower because the original Libertyville DS contained a very low concentration of orthophosphate.

A few experiments were performed in the continuous flash chamber to determine if the $CO_2$ present in DS could be removed at a faster rate and to a lower residual concentration than that possible by heat treatment alone. All the experiments were performed following the same basic procedure. Digester supernatant was transferred to the reactor where it was heated to 65°C. In one example, the DS was immediately flashed after it reached 65°C. In the other two cases, the DS was maintained at 65°C for either 15 minutes or two hours. The heated DS was transferred to the vacuum chamber by suction, as a continuous stream. A schematic of the vacuum chamber is shown in figure 17. The volume maintained in the vacuum chamber was one half gallon. The DS was discharged through a sparger into the chamber which was operated at a vacuum 23" of mercury. The volume in the chamber was maintained constant by pumping out the DS at a predetermined rate. The average retention time within the chamber was approximately 2 minutes. All the experiments demonstrated that the residual concentration of $CO_2$ could not be significantly lowered by flashing the DS under these operating conditions.

It was observed, however, that the nitrogen concentration was affected by such treatment. In Table XV can be seen nitrogen analyses for samples treated by heat alone and by heat and vacuum. The data confirms the observations made during the bench scale experiments.

## EFFLUENT QUALITY

The quality of the process effluent depends on the original concentration of impurities present in the digester supernatant and the efficiency of the liquid-solid separation after treatment by either chemicals or heat.

In Table XVI can be seen some examples of the differences in original composition of digester supernatant samples used in our research. They represent samples from the Libertyville and the Lake Zurich sewage treatment plants.

The quality of the effluent was first determined under optimum conditions in the laboratory scale equipment. All the experiments in this section were performed with digester supernatant obtained at the

TABLE XIV

PRECIPITATION OF PHOSPHATE FROM DIGESTER SUPERNATANT BY HEAT TREATMENT - 80°C CONTINUOUS RUNS

(LAKE ZURICH SEWAGE TREATMENT PLANT)

| Exp. No. | Volume in Reactor(gal) | Retention Time(min) | Original pH | Original OP (mg/l) | Original TP (mg/l) | Original $CO_2$ (mg/l) | Original COD (mg/l) | Original SS (mg/l) | Treated pH | Treated OP (mg/l) | Treated TP (mg/l) | Treated $CO_2$ (mg/l) | Treated COD (mg/l) | % Removal OP | % Removal TP | % Removal $CO_2$ | % Removal COD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1(1) | 6 | 15 | 7.4 | 46 | 67 | - | 1020 | 720 | 9.0 | 11 | 13 | - | 540 | 76 | 81 | - | 47 |
| | | | | | | | | | 9.3 | 7 | 9 | - | 480 | 85 | 87 | - | 52 |
| | | | | | | | | | 9.3 | 6 | 8 | - | 450 | 87 | 88 | - | 56 |
| 2 | 6 | 15 | 7.5 | 85 | 109 | 2165 | 2333 | 2220 | 8.6 | 11 | 16 | 1120 | 1240 | 87 | 85 | 48 | 47 |
| | | | | | | | | | 9.1 | 8 | 11 | 1040 | 1190 | 91 | 90 | 52 | 49 |
| | | | | | | | | | 9.1 | 8 | 11 | 1050 | 1140 | 91 | 90 | 51 | 51 |
| | | | | | | | | | 9.1 | 8 | 11 | 1070 | 1120 | 91 | 90 | 50 | 52 |
| | | | | | | | | | 9.1 | 8 | 11 | 1030 | 1100 | 91 | 90 | 52 | 53 |
| 3 | 15 | 45 | 7.4 | 57 | 87 | 2200 | 2180 | 1440 | 8.9 | 10 | 13 | 1370 | 1090 | 82 | 85 | 38 | 50 |
| | | | | | | | | | 8.9 | 9 | 11 | 1320 | 1060 | 84 | 87 | 40 | 51 |
| | | | | | | | | | 9.0 | 9 | 11 | 1140 | 1110 | 84 | 87 | 48 | 49 |
| | | | | | | | | | 9.0 | 8 | 11 | 1170 | 1090 | 86 | 87 | 46 | 50 |
| | | | | | | | | | 8.9 | 9 | 11 | 1320 | 1040 | 84 | 87 | 40 | 52 |

(1) Sample of DS obtained from the Libertyville Sewage Treatment Plant

OP - Orthophosphate Phosphorus
TP - Total Phosphorus
COD - Chemical Oxygen Demand
SS - Suspended Solids

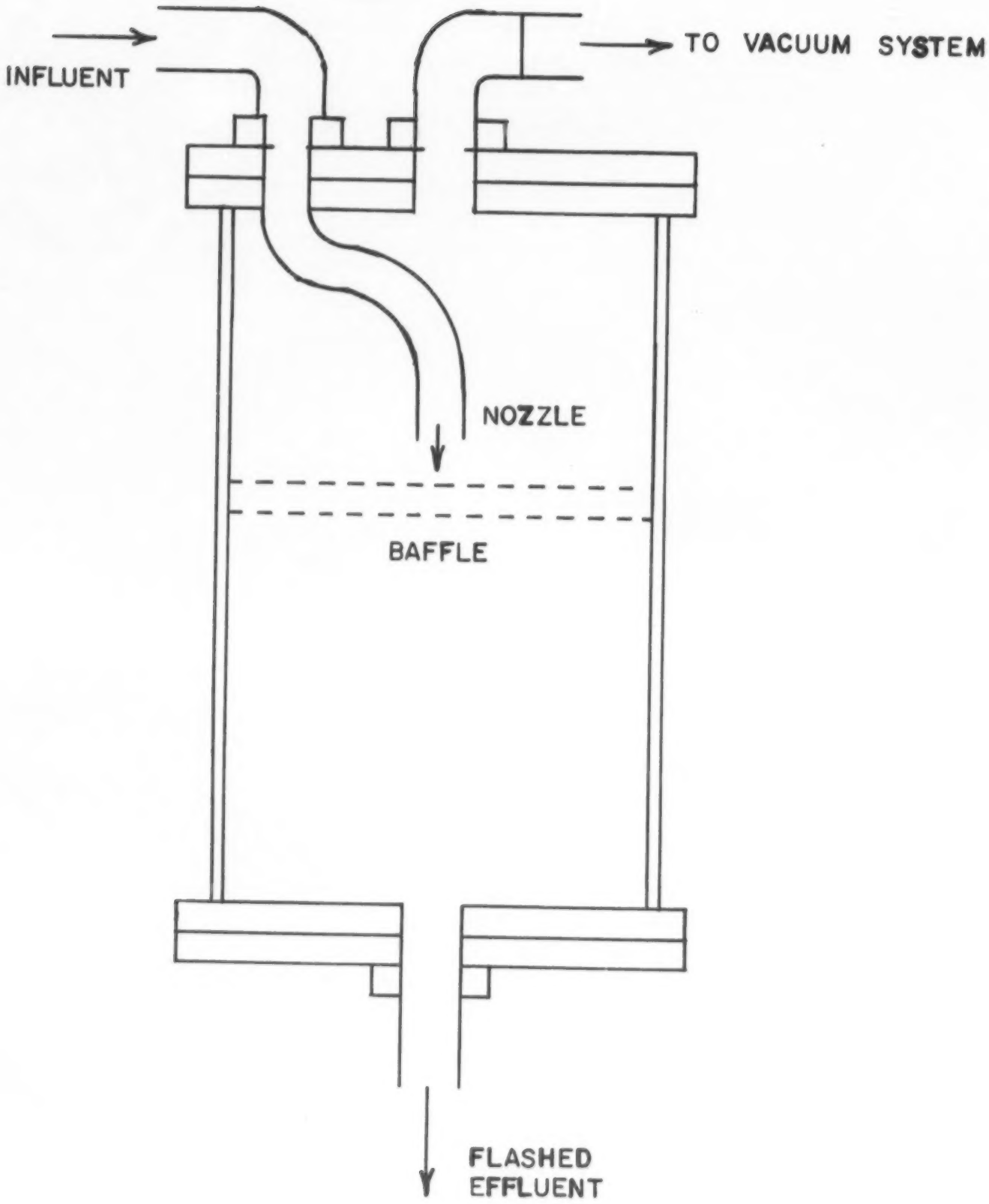



FIGURE 17 SCHEMATIC OF THE FLASH CHAMBER

TABLE XV

RESIDUAL CONCENTRATION OF NITROGEN IN DIGESTER SUPERNATANT TREATED BY HEAT AND/OR HEAT AND VACUUM (LAKE ZURICH SEWAGE TREATMENT PLANT)

| Temp. (0°C) | Vacuum (inches of Hg) | Original | | Treated | | % Removal | |
|---|---|---|---|---|---|---|---|
| | | TN | $NH_3$ as N | TN | $NH_3$ as N | TN | $NH_3$ as N |
| | | (mg/l) | | (mg/l) | | (mg/l) | |
| 65 | - | 684 | 532 | 586 | 517 | 15 | 3 |
| 70 | - | 642 | - | 544 | - | 16 | - |
| 80 | - | 656 | - | 492 | - | 25 | - |
| 65 | 23 | 684 | 532 | 369 | 290 | 47 | 46 |

TN - Total Nitrogen

TABLE XVI

COMPOSITION OF THREE TYPICAL DIGESTER SUPERNATANT SAMPLES FROM THE LIBERTYVILLE AND LAKE ZURICH SEWAGE TREATMENT PLANTS

| | Libertyville | | | Lake Zurich | | |
|---|---|---|---|---|---|---|
| Total P (mg/1) | 70 | 82 | 67 | 87 | 92 | 102 |
| Orthophosphate P (mg/1) | 71 | 73 | 46 | 57 | 61 | 62 |
| COD (mg/1) | 673 | 560 | 1020 | 2180 | 2060 | 2340 |
| Total N (mg/1) | 378 | 330 | 452 | 656 | 590 | - |
| Suspended Solids (mg/1) | - | - | 720 | 1440 | 1100 | 1700 |

Libertyville plant. Analyses of the effluents were studied after treatment of the DS by 3 methods, namely (1) with magnesite and sodium hydroxide, (2) with magnesium carbonate, and (3) with heat or heat and vacuum. In all cases, the solids were separated from the liquid phase by centrifugation in a batch type centrifuge.

In Table XVII can be seen the analyses for treated DS after precipitation of phosphate was obtained by addition of calcined magnesite and sodium hydroxide (for final pH adjustment). It is obvious that the quality of the digester supernatant liquor can be greatly improved by precipitation with magnesia. Phosphate concentration is reduced together with the concentration of BOD, COD and the nitrogen. The residual total nitrogen decreases with increases of magnesium ion concentration.

Analysis of a sample of DS treated with magnesium carbonate without final pH adjustment with a soluble base can be seen in Table XVIII. The magnesium concentration used was stoichiometric with respect to phosphate. The treated DS contained a substantially reduced concentration of BOD and COD as well as phosphate. In this instance, however, only a small amount of nitrogen was removed.

In Table XIX can be seen the analyses of DS treated with heat or heat and vacuum under different operating conditions. From the data it may be concluded that a treatment at 65°C with or without vacuum yields an effluent substantially cleaner than the original digester liquor. Two of the most deterimental impurities, phosphorus and nitrogen, can be reduced to very low concentrations.

Additional experiments were performed using the treated digester liquor from the Lake Zurich sewage treatment plant. The DS from this plant was always higher in suspended solids, nitrogen, COD and total phosphorus than the Libertyville DS. All the treated samples for the solid-liquid separation experiments were obtained from the pilot plant runs.

First, filtration was tested for the liquid-solid separation. An Eimco filtration kit and procedure were used in these experiments. The preliminary observations demonstrated that filtration is not a practical method to obtain the desired effluent quality. The very fine organic and inorganic solids present in the DS blind the filter cloth quite rapidly. This approach was abandoned because it would be extremely expensive.

Clarification by settling appears to be a practical solution to the liquid-solid separation problem. A solids contact clarifier as manufactured by the Eimco or Dorr Oliver Companies should be quite suitable for this application. Addition of polymers to improve the speed and efficiency of the liquid-solid separation should be evaluated. The size of the equipment used in the pilot plant studies, precluded any serious evaluation of liquid-solid separation by settling on a pilot scale.

Jar test experiments were performed to determine the type of polymer most suitable for this application. It was found that the best results

TABLE XVII

ANALYSIS OF CHEMICALLY TREATED DIGESTER SUPERNATANT
FROM THE LIBERTYVILLE PLANT - pH 9.0

| | | Treatment | | |
|---|---|---|---|---|
| | Original | MgO+NaOH 0.2 (1) | MgO+NaOH 0.4 (2) | MgO+NaOH 1.0 (3) |
| Total P (mg/1) | - | 6 | 5 | 6 |
| Orthophosphate P (mg/1) | 82 | 7 | 5 | 5 |
| BOD (mg/1) | 315 | - | - | 64 |
| COD (mg/1) | 360 | 280 | 281 | 341 |
| Total N (mg/1) | 413 | 326 | 318 | 298 |

(1) Amount of $Mg^{++}$ added = 20% of stoichiometry

(2) Amount of $Mg^{++}$ added = 40% of stoichiometry

(3) Amount of $Mg^{++}$ added = stoichiometry

TABLE XVIII

ANALYSIS OF DIGESTER SUPERNATANT BEFORE AND AFTER PHOSPHATE PRECIPITATION WITH MAGNESIUM CARBONATE (LIBERTYVILLE PLANT)

| | Original | Treated |
|---|---|---|
| Total P (mg/l) | 70 | 5(1) |
| Orthophosphate P (mg/l) | 71 | 9 |
| BOD (mg/l) | 234 | 53 |
| COD (mg/l) | 673 | 280 |
| Total N (mg/l) | 378 | 336 |

(1) The analysis for P was made several days after the experiment was performed. It is lower than the orthophosphate concentration probably due to phosphate post precipitation upon standing.

TABLE XIX

ANALYSIS OF DIGESTER SUPERNATANT TREATED WITH HEAT OR HEAT AND VACUUM (LIBERTYVILLE PLANT)

| Experiment No. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Temperature (°C) | 40 | 65 | 65 | 65 |
| Vacuum (27" Hg) | yes | no | yes | yes |
| Retention Time (min.) | 60 | 120 | 60 | 60 |
| Total P (mg/1) | 9 | 4 | 2 | 2 |
| Orthophosphate P (mg/1) | 9 | 4 | 1 | 1 |
| BOD (mg/1) | 134 | 86 | - | - |
| COD (mg/1) | 268 | 340 | 139 | 214 |
| Total N (mg/1) | 319 | 45 | 8 | 16 |

were obtained with a cationic polyethyleneimine polymer. When a dose of 6 mg/l of active polymer was added 89% of the suspended solids were removed from the liquid phase. Visual observation of the polymer treated sample of DS was similar in quality to the centrifuged DS sample.

Centrifugation was tested because it appears to be a good method for high speed liquid-solid separation. Initial centrifugation tests were made using a Sharples high speed centrifuge operating at 13,200 g. The unit, which was a small bench type model was fed at increasing rates ranging from 280 ml/min to 2,500 ml/min. Table XX shows the analytical results of two runs with treated DS from the Lake Zurich plant. As shown, this centrifuge performs more effectively when magnesia is used to treat the digester liquor. The density of the solids is higher and therefore, they are easier to separate from the liquid phase. Lower flow rates are required when the DS is only heat treated. The magnesia treated samples indicate a dramatic reduction in total phosphate, orthophosphate and suspended solids.

A Sharples-Fletcher Mark III continuous centrifuge was also tested. A photograph of the pilot scale centrifuge is shown in Figure 18. All the experiments were performed at a rotation of 2,550 rpm. The flow rate varied from 300 to 730 ml/min. Table XXI shows the results of these tests. The quality of the effluent produced by the Mark III centrifuge is acceptable. Centrifugation should be considered as a means of liquid-solid separation and should be evaluated for longer periods to establish reliability of performance.

## PRODUCT CHARACTERIZATION

The solids precipitated from a waste stream of a sewage plant may vary in composition depending on the impurities present in solution and in suspension. If the waste stream under consideration contains a low concentration of calcium, then it is anticipated that the ammonia nitrogen and orthophosphate initially present will precipitate with magnesia as a mixture of $MgNH_4PO_4 \cdot 6H_2O$ and $Mg_3(PO_4)_2 \cdot 4H_2O$. On the other hand, in the presence of a high concentration of calcium, precipitation of the orthophosphate and ammonia nitrogen by addition of magnesia will yield a mixture of $MgNH_4PO_4 \cdot 6H_2O$, $Mg_3(PO_4)_2 \cdot 4H_2O$ and $Ca_3(PO_4)_2$.

The water of the Libertyville and Lake Zurich sewage plants contain a high concentration of both calcium and magnesium. In order to predict the type of product that might be precipitated from such a stream, phosphate precipitation was first performed in a synthetic mixture containing 100 mg/l P, 117 mg/l Mg, and 114 mg/l Ca. The analysis of the precipitate is shown in Table XXII. Calculated composition of this precipitate is as follows: 15.6% $MgNH_4PO_4 \cdot 6H_2O$, 45.0% $Mg_3(PO_4)_2 \cdot 4H_2O$ and 36.8% $Ca_3(PO_4)_2$. Approximately 10% of the total phosphate is chemically associated with the nitrogen.

Analysis of several solids precipitated from digester supernatant collected at the Libertyville plant are shown in Table XXIII. These

TABLE XX

CENTRIFUGATION OF DIGESTER SUPERNATANT WITH A SHARPLES HIGH SPEED (13,200 g) CENTRIFUGE (LAKE ZURICH SEWAGE TREATMENT PLANT)

| Treatment | Flow Rate (ml/min.) | Original (mg/l) TP | OP | SS | Effluent (mg/l) TP | OP | SS | % Recovery TP | OP | SS |
|---|---|---|---|---|---|---|---|---|---|---|
| $Mg(OH)_2$ (70 mg/l Mg, pH 9.0) | 280 | 93 | 76 | 1640 | 5 | 2 | 80 | 97 | 95 | 95 |
| | 1560 | 93 | 76 | 1640 | 10 | 5 | 211 | 93 | 89 | 87 |
| | 2480 | 93 | 76 | 1640 | 11 | 5 | 560 | 93 | 88 | 66 |
| Heat 65°C | 660 | 100 | 80 | 2500 | 20 | 11 | 520 | 80 | 86 | 79 |
| | 750 | 100 | 80 | 2500 | 31 | 24 | 860 | 79 | 70 | 66 |

TP - Total Phosphorus
OP - Orthophosphate Phosphorus
SS - Suspended Solids

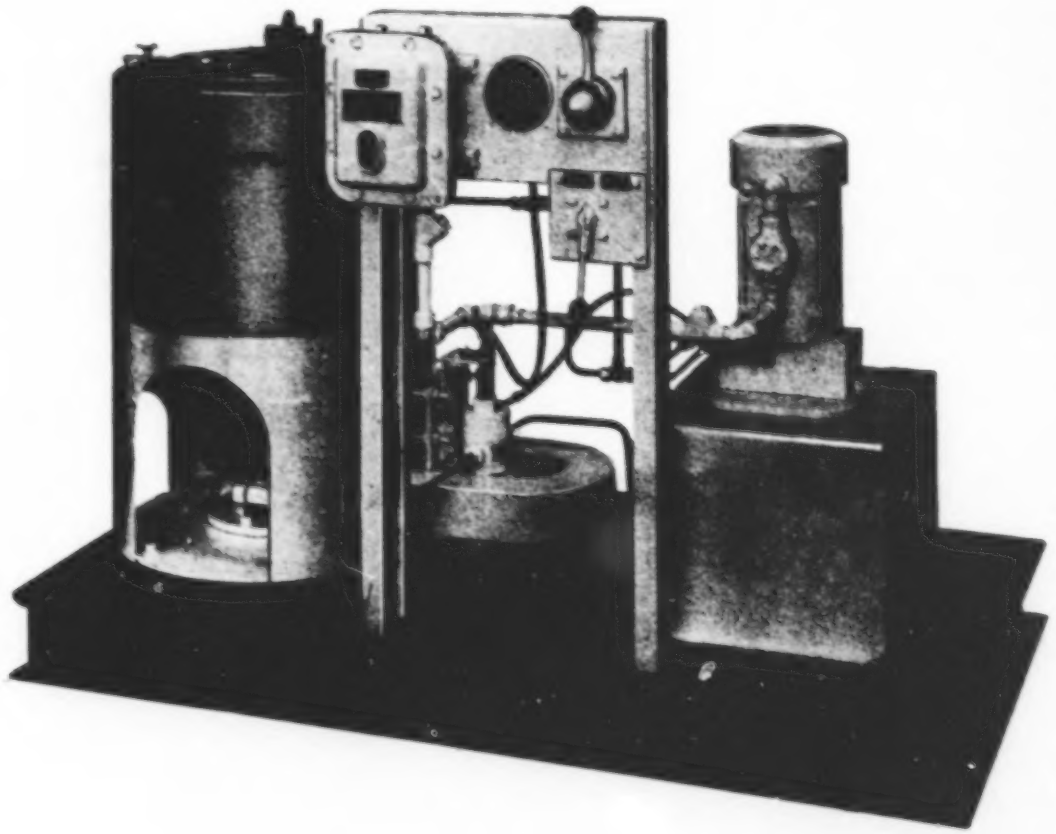


FIGURE 18 PHOTOGRAPH OF THE PILOT SCALE CONTINUOUS CENTRIFUGE

TABLE XXI

CENTRIFUGATION OF DIGESTER SUPERNATANT WITH A CONTINUOUS SHARPLES-FLETCHER MARK III CENTRIFUGE (2,550 rpm) (LAKE ZURICH SEWAGE TREATMENT PLANT)

| Treatment | Flow Rate (ml/min.) | Original (mg/l) | | | Effluent (mg/l) | | | % Recovery | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | TP | OP | SS | TP | OP | SS | TP | OP | SS |
| Heat (65°C) | 300 | 121 | 76 | 3160 | 19 | 15 | 60 | 84 | 80 | 98 |
| | 730 | 121 | 76 | 3160 | 24 | 21 | 460 | 80 | 72 | 85 |
| $Mg(OH)_2$ (70 mg/1 Mg, pH 9.0) | 450 | 93 | 76 | 1640 | 16 | 10 | 280 | 83 | 87 | 83 |

TP - Total Phosphorus
OP - Orthophosphate Phosphorus
SS - Suspended Solids

TABLE XXII

ANALYSIS OF SOLIDS PRECIPITATED IN A SYNTHETIC SYSTEM (pH 9.5)

| | % Composition |
|---|---|
| Total $P_2O_5$ | 43.3 |
| Available $P_2O_5$* | 43.3 |
| Total N | 0.9 |
| Ca | 14.3 |
| Mg | 11.3 |

*Available to growing plants according to tests of Association of Official Agricultural Chemists (AOAC).

TABLE XXIII

ANALYSIS OF SOLIDS PRECIPITATED FROM DIGESTER SUPERNATANT OBTAINED AT THE LIBERTYVILLE SEWAGE TREATMENT PLANT

| Treatment | Stoichiometry* | Final pH | % Total $P_2O_5$ | % Avail. $P_2O_5$** | % Total N | % $NH_3$ N |
|---|---|---|---|---|---|---|
| MgO+NaOH | 0.4 | 9.0 | 21.48 | 21.08 | 3.35 | - |
| MgO+NaOH | 0.4 | 10.0 | 23.47 | 23.08 | 2.73 | 0.62 |
| MgO+$NH_4OH$ | 0.4 | 9.5 | 29.48 | 28.60 | 2.44 | - |
| MgO+$NH_4OH$ | 1.0 | 9.5 | 21.70 | 20.50 | 2.60 | 1.00 |
| MgO+NaOH | 1.0 | 10.0 | 20.65 | 20.38 | 1.86 | - |
| 70°C | - | 8.9 | 19.51 | 19.41 | 3.61 | - |
| 65°C | - | 8.9 | 17.58 | 17.40 | 2.46 | - |

*Magnesium relative to phosphorus

**Available to growing plants according to AOAC test

solids are approximately 50% lower in phosphate concentration than those recovered from the synthetic system. This is expected because the concentration of suspended solids present in the DS used was approximately 500 mg/l and the phosphate solids recovered from a synthetic system are also approximately 500 mg/l. Therefore, there is a 50% dilution of the phosphates obtained from the DS with extraneous solids. The nitrogen content of the solids precipitated from the DS is much higher than the concentration found in the synthetic system i.e., from 2.0% - 3.0% N in the DS solids compared to 0.9% N in the synthetic system. This is due to the fact that organic nitrogen compounds which are suspended in the DS are precipitated together with the phosphate.

It is significant to note that most of the phosphate is present in a form available to plants, i.e., passes the solubility test established by the AOAC procedure (Association of Official Agricultural Chemists).

An attempt to identify the phosphate mixture by X-ray techniques indicated that the solids are amorphous. It was observed, however, that during the precipitation procedure, a crystalline phase could be separated from the bulk of the solids. This crystalline material identified by X-ray as $MgNH_4PO_4 \cdot 6H_2O$.

Table XXIV summarizes the data on the solids collected from pilot plant runs performed at the Lake Zurich sewage treatment plant. The digester supernatant tested at Lake Zurich contained on an average 1500 mg/l suspended solids. If the DS did not contain any inert solids, then the theoretical concentration of total $P_2O_5$ would be 43% as shown in Table XXII. The theoretical amount of phosphate solids which would be precipitated is 500 mg/l. Suspended solids present in the digester should dilute the phosphate precipitate approximately by a factor of 4 and therefore the average percent $P_2O_5$ expected is 10.7%. The results in Table XXIV indicate that solids containing from 10% to 15% $P_2O_5$ may be recovered from Lake Zurich digester supernatant. In all cases the phosphate is present in a form available to plants. The nitrogen content is 3% in most cases.

TABLE XXIV

ANALYSIS OF SOLIDS PRECIPITATED FROM DIGESTER SUPERNATANT OBTAINED AT THE LAKE ZURICH SEWAGE TREATMENT PLANT

| Treatment | % Total $P_2O_5$ | % Available (1) $P_2O_5$ | % Total N |
|---|---|---|---|
| NaOH (pH 8.9) | 10.5 | 10.1 | 2.8 |
| $NH_4OH$ (pH 10.0) | 10.7 | 10.3 | 4.0 |
| 65°C (60 min. retention time) | 13.5 | 13.3 | 3.3 |
| 65°C (90 min. retention time) | 10.9 | 10.7 | 3.1 |
| 65°C (30 min. retention time) | 12.9 | 12.6 | 3.5 |
| 70°C (45 min. retention time) | 14.0 | 13.6 | 3.3 |
| 75°C (retention time) | 15.2 | 14.7 | 3.5 |

(1) Available to growing plants according to AOAC test.

# SUMMARY AND CONCLUSIONS

1. Precipitation of orthophosphate from digester supernatant may be accomplished by adding either a soluble salt of magnesium, magnesium oxide, magnesium hydroxide or magnesium carbonate. The efficiency with which phosphate is removed depends on the reactivity of the magnesium source, when an insoluble compound is used, and on the final pH of precipitation. A pH range between 9.0 and 9.5 yields the highest phosphate removal. When a final pH adjustment is required either ammonium hydroxide or sodium hydroxide may be used for final neutralization. Variables such as seed recycle, retention time and speed of agitation do not have a significant effect when precipitation is obtained by addition of magnesium ion and pH adjustment.

2. Precipitation of orthophosphate from digester supernatant may be accomplished by addition of a soluble neutralizing base such as ammonium hydroxide or sodium hydroxide. In areas where hard water exists, the digester supernatant contains sufficient cations such as calcium and magnesium to precipitate the orthophosphate.

3. A new process for the precipitation of orthophosphate from digester supernatant, based on the heat decomposition of ammonium bicarbonate was tested on a bench and pilot scale. As the ammonium bicarbonate decomposes, $CO_2$ evolves from the system causing a raise in pH. Precipitation of calcium and magnesium phosphate is obtained without need of chemical additives.

4. Phosphate precipitation by all the processes described improves the quality of the treated stream because it removes a very high percentage of phosphate and substantial amounts of nitrogen and COD.

5. All the processes were tested at both bench and pilot plant levels.

6. On the average a removal of 85 to 90 percent of the phosphate present in digester supernatant may be expected, without addition of chemicals.

7. A mixture of $MgNH_4PO_4 \cdot 6H_2O$ and $Mg_3(PO_4)_2 \cdot 4H_2O$ will precipitate from a stream substantially free of calcium. If calcium is present in high concentrations, then a mixture of $MgNH_4PO_4 \cdot 6H_2O$, $Mg_3(PO_4) \cdot 4H_2O$ and $Ca_3(PO_4)_2$ is precipitated.

8. The percent composition of the solids is dependent on the amount of inert impurities suspended in the original digester supernatant and in the relative concentrations of magnesium and calcium present or added to the system.

9. From the Libertyville sewage plant streams, it is anticipated that the solids precipitated will contain approximately 20% $P_2O_5$ and 2% nitrogen. From the Lake Zurich sewage plant, solids containing 12% $P_2O_5$ and 3% nitrogen may be recovered.

## PATENTS

During the course of the work on Contract No. 14-12-171, several technical discoveries were made which may be novel and patentable. In accordance with the Contract, disclosures of invention on three of these were submitted to FWPCA.

1. Disclosure Number FWP-1533. The novel features of this invention are as follows: A high total phosphate removal and substantial removal of nitrogen, COD, and BOD can be accomplished by decomposition of the ammonium bicarbonate present in the digester supernatant. The decomposition may be achieved by increasing the temperature, by reducing the pressure or by a combination of these two variables. A high degree of agitation or other means of exposing a large surface (i.e., spraging) increases the speed of decomposition. The resulting solids are high in phosphate concentration in a form available to growing plants. The process may be operated continuously.

2. Disclosure Number FWP-1669. The novel features of this invention are as follows: A high total phosphate removal can be accomplished by increasing the pH of digester supernatant with ammonium hydroxide to approximately 10.0. Phosphate precipitates as calcium phosphate and/or magnesium ammonium phosphate. The precipitated solids are separated from the liquid phase. The treated DS now free of phosphate is flashed under vacuum or air stripped, thus releasing ammonia which is recycled back to the incoming raw DS.

3. Disclosure Number FWP-1679. The novel features of this invention are as follows: Chemical purification of sewage is based on the precipitation of orthophosphate and ammonia nitrogen as magnesium ammonium phosphate. In sewage water the ratio of nitrogen as N to orthophosphate as P is approximately 4 to 1 on a mol basis. In order to remove all the phosphate and nitrogen, an amount of phosphate is added to the sewage, in the form of triple superphosphate (a low cost phosphate source), to be stoichiometrically equivalent to the excess nitrogen. When the sewage containing the balanced amount of phosphate and ammonia nitrogen is neutralized with magnesia, precipitation of $MgNH_4PO_4$ removes the undesirable impurities N and P in an insoluble form. The solid product recovered has fertilizer value and contains in addition to the magnesium ammonium phosphate, calcium phosphate, and solid organic impurities of varied composition. The liquid phase which contains water soluble organic materials and polyphosphate is percolated through a charcoal bed prior to discharge. The spent charcoal may be regenerated for reuse by known processes.

# REFERENCES

1. Dunseth, M. G. and Salutsky, M. L., "Removal of Scale Forming Elements from Sea Water," Ind. Eng. Chem. 56, 56-61 (1964).

2. Salutsky, M. L. and Messina, P., "Removal of Scale Formers with By-Product Recovery," Proc. First Internat'l. Sym Water Desaln., Vol. 2, Washington, D. C., 1965, pp 695-707.

3. Bridger, G. L., Salutsky, M. L., and Starostka, R. W., "Metal Ammonium Phosphates as Fertilizer," J. Agr. Food Chem. 10, 181-8 (1962).

4. Lunt, O. R., Kofranek, A. M., and Clark, S. B., "Availability of Minerals from Magnesium Ammonium Phosphates," J. Agr. Food Chem., 12, 497-504 (1964).

5. Shea, T., "Progress Report on Studies on Removal of Carbonaceous Nitrogenous and Phosphorus Materials from Concentrated Waste Streams," pending FWPCA Report (May 1969).

6. Fisher, R. A., "Progress Report, Phase I, Development of a Process to Remove Carbonaceous, Nitrogenous and Phosphorus Materials from Anaerobic Digester Supernatant and Related Process Streams," FWPCA Report (May 1969).

7. Kappe, S. E., "Digester Supernatant Problems, Characteristics and Treatment," Sew. and Indust. Wastes, 30, 7, 937, July (1958).

8. Barth, E. F., et al., "Chemical Control of Nitrogen and Phosphorus in Wastewater Effluent," Jour. WPCF, 40, 12, 2040 (Dec. 1968).

9. Rawn, A. M., et al., "Multiple-Stage Sewage Sludge Digestion," Trans. Amer. Soc. Civil Eng., 104, 93 (1939).

10. Bube, K., "Uber Magnesiumammonium phosphat," Z. Anal. Chem., 49, 525-96 (1910).

11. Szekeres, L. and Rady, M., "The Solubility of Some Calcium Phosphates," Ind. Eng. Chem., Anal. Ed. 18, 699-702 (1946).

12. Uncles, R. F. and Smith, G. B. L., "Solubility of Magnesium Ammonium Phosphate Hexahydrate," Ind. Eng. Chem., Anal. Ed. 18, 699-702 (1946).

13. Ries, K. M., Dunseth, M. G., Salutsky, M. L., and Shapiro, J. J., "Ultimate Disposal of Phosphate from Waste Water by Recovery as Fertilizer, Phase I - Final Report," FWPCA Report, Contract No. 14-12-171 (July 15, 1969).

# APPENDIX

## ANALYTICAL METHODS

### Orthophosphate (OP)

Orthophosphate concentration was determined using aminonaphtholsulfonic acid method in accordance with Standard Methods. The sample was centrifuged 3474 gravity-minutes, and the centrate was then filtered through an 8μ membrane filter, 47 mm diameter. The filtrate was diluted with deionized water from 40:1 to 200:1 depending on the suspected concentration. A blue color was developed by using ammonium molybdate-acid reagent and aminonaphtholsulfonic acid. The blank used was the diluted filtrate treated only with the aminonaphtholsulfonic acid reducing reagent. The color was allowed to develop for five minutes, and the color intensity was measured on a Hach Direct Read colorimeter using a Hach #5330 color filter.

### Total Phosphorus (TP)

Total phosphorus was determined using the nitric acid wet ash procedure. The sample was digested at a low temperature in nitric acid until the sample almost attained dryness. The resulting slurry was redissolved in hydrochloric acid and boiled for 15 minutes. The resulting solution was diluted with deionized water from 40:1 to 400:1 depending on the suspected concentration. Color was developed according to the above procedure for orthophosphate.

### Total Solids (TS)

Total solids were determined in accordance with Standard Methods by weighing the residue after 100 ml of the sample had been dried at 103°C for approximately 20 hours. All gravimetric determinations were made using a Mettler H-6 four place analytical balance.

### Suspended Solids (SS)

Suspended solids were determined by filtering from 10 to 100 ml of the sample, depending on the suspended solids concentration, through a 0.45 micron membrane filter. The suspended matter removed by filter was dried at 103°C for two hours and weighed. This procedure is in accordance with Standard Methods.

### Total Kjeldahl Nitrogen (TKN)

Total Kjeldahl nitrogen was determined by digesting 100 ml of the sample in sulfuric acid, in the presence of mercury, until the sample was clear. The digested sample was made alkaline with sodium hydroxide in the presence of sodium thiosulfate and the ammonia was distilled into 50 ml 0.1N sulfuric acid. The residual sulfuric acid was titrated with 0.1N sodium hydroxide to the methyl red endpoint. The distillation was performed in a Kjeldahl distillation unit.

Chemical Oxygen Demand (COD)

Chemical oxygen demand was determined in accordance with Standard Methods. On the average, the sample was analyzed 36 hours after it was collected. The sample was refluxed for 2 hours in a known amount of potassium dichromate and sulfuric acid. Mercuric sulfate was used to eliminate chloride interference. Silver sulfate was added as a catalyst in the refluxing. The excess dichromate was titrated with ferrous ammonium sulfate.

Total Alkalinity as $CaCO_3$

Total alkalinity was determined in accordance with Standard Methods. 50 ml of sample was titrated with N/50 sulfuric acid to the methyl orange endpoint. The alkalinity was expressed as mg/l $CaCO_3$.

Carbon Dioxide ($CO_2$)

Carbon dioxide was determined by the titrimetric method in accordance with Standard Methods. The sample was titrated with N/100 sodium hydroxide to pH 8.3, using a pH meter.

Biochemical Oxygen Demand (BOD)

The method used in the determination of BOD was in accordance with Standard Methods. The incubation of sample for BOD started within 2 hours after collection. All samples were seeded and dilutions were incubated for 5 days at 20°C. Initial and final dissolved oxygen determinations were made using the azide modification of the Winkler Method.

Ammonia Nitrogen

Ammonia nitrogen was determined similar to the TKN except that prior to distillation the sample was not digested.

pH

pH was measured using a Beckman Expandomatic pH meter. A general purpose glass electrode and a fiber junction calomel electrode were used.

Oxidation-Reduction Potential (ORP)

All oxidation-reduction potential measurements were made on a Beckman Expandomatic pH meter using a fiber junction calomel electrode and a platinum electrode. ORP corrected for calomel reference.

Disssolved Oxygen (DO)

All dissolved oxygen measurements, except those used in BOD calculations were measured on a Precision Scientific galvanic cell. oxygen analyzer.

Percent Solids

Percent solids was determined on an Ohaus moisture balance.

Calcium (Ca) and Magnesium (Mg)

Calcium and magnesium concentrations were determined using atomic absorption. The sample was digested in hydrochloric acid. Lanthanum chloride was added to mask the phosphate. Hydrogen was used as a fuel and air was the oxidant. The calcium was determined at 4227 angstroms and the magnesium was determined at 2852 angstroms.

X-ray Diffraction

All X-ray diffraction used the powder diffraction technique.

Association of Official Agricultural Chemists (AOAC) Analytical Procedures - (These procedures were used for the analysis of solid products.)

Analyses in accordance with these procedures were run only on precipitated solids reocvered from the precipitation research.

Total Nitrogen by Kjeldahl

Sample containing nitrogen is digested with concentrated sulfuric acid. The digested clear sample is distilled in the presence of excess sodium hydroxide. The liberated ammonia in the distillate is collected in a standard acid. The excess of acid is titrated with a standard base. Methyl red indicator is used to detect the endpoint.

Total Phosphorus

Total phosphorus was determined by heating the sample in potassium nitrate and nitric acid until dry. The evaporated residue is ignited and then redissolved in deionized water and hydrochloric acid. The phosphorus concentration of this solution is determined by using the aminonaphthol-sulfonic acid reducing reagent method of orthophosphate determination.

Available Phosphorus

Available phosphorus was determined by placing the sample on filter paper and washing it with deionized water. The residue on the paper is added to hot ammonium citrate. The ammonium citrate solution is then filtered and washed with deionized water. The two filtrates are combined and the phosphorus concentration is determined according to the procedure for total phosphorus.

## Water Soluble Phosphorus

The procedure for determining water soluble phosphorus was the same as that used for available phosphorus except that the residue on the filter paper was not digested in ammonium citrate.

## Calcium

Calcium was determined by heating the sample in potassium nitrate and nitric acid until dry. The evaporated residue was ignited and then redissolved in deionized water and hydrochloric acid. Ferric chloride was added and the sample was then neutralized with ammonium hydroxide. Sodium acetate was added and the sample was digested and filtered. The calcium concentration in the filtrate was determined by titration with 0.1 M EDTA to the Erichrom Black T endpoint.

## Magnesium

Magnesium was determined by the same method as calcium, except that the filtrate was digested with ammonium oxalate. The solution is buffered to pH 10.0 and titrated with 0.1 M EDTA to the Erichrom Black T endpoint.



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